



FEMMS '07

Program and Abstracts for
The Eleventh Frontiers of Electron
Microscopy in Materials Science 2007

September 23-28, 2007
Sonoma DoubleTree Hotel

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FEMMS '07

Frontiers of Electron Microscopy in Materials Science 2007

Sonoma DoubleTree Hotel, Rohnert Park, Calif.

September 24-28, 2007

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Frontiers of Electron Microscopy in Materials Science 2007
Sonoma DoubleTree Hotel, Rohnert Park, Ca.
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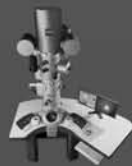
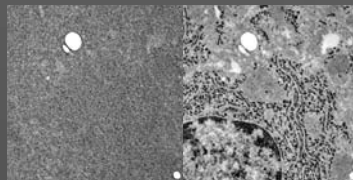
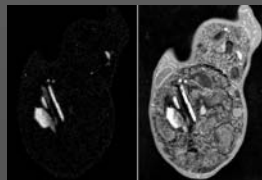
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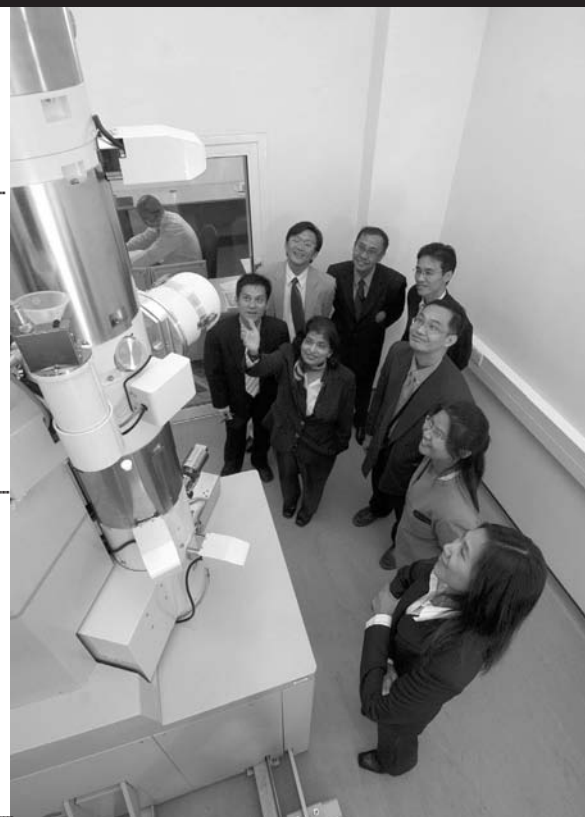
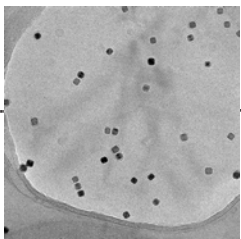
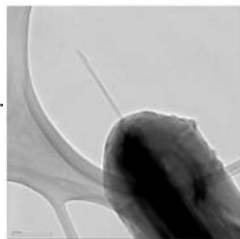
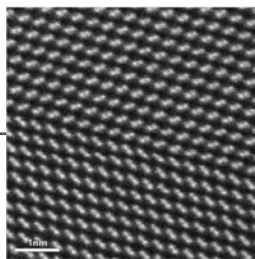
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Sunday	Library	16:00 - 20:00
Monday	Salon III-IV	07:30 - 17:30
Tuesday	Salon III-IV	07:30 - 17:30
Wednesday	Salon III-IV	07:30 - 12:00
Thursday	Salon III-IV	07:30 - 17:30
Friday	Salon III-IV	07:30 - 12:00

Logistics

Monday Friday	All Sessions	Salon III - IV
Monday	Lunch	Upper Patio
Monday	Dinner	Vinyard Room
Monday	Reception and Poster Session	Chardonnay Room
Tuesday	Lunch	Upper Patio
Tuesday	Reception	Upper Lobby
Tuesday	Dinner	Vineyard Room
Thursday	Lunch	Vineyard Room
Thursday	Reception	Upper Lobby



Professor Mick Brown, FRS

Mick Brown is an Emeritus Professor of Physics at the Cavendish Laboratory, Cambridge, and was elected as a Fellow of the Royal Society in 1982. His research interests are in solid state physics and electron microscopy. With his students he developed Scanning Transmission Electron Microscopy, and used it to tackle many problems in the science of materials, including nanodiffraction from disordered materials, the distribution of nitrogen in diamond, helium bubbles in irradiated steels, and the measurement of bandgaps by EELS. He took the initiative which led to the foundation of the Daresbury SuperSTEM laboratory for aberration-corrected dedicated STEM.

He is currently writing a book about dislocation plasticity. In recent years he has been concerned about the presentation of science, particularly physics, at both secondary and tertiary levels. He participated in the Institute of Physics 16-19 initiative, which led to the production of 'Advancing Physics'; also in the Undergraduate Physics Enquiry, which led to the formation of the 'New Degree Working Group', which he chaired. These activities led to the introduction of new interdisciplinary physics degrees in several British universities.

Sessions

Monday AM - High Resolution Imaging ***Ulrich Dahmen and Stephen Pennycook, Chairs***

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8:50	Welcome to Conference	Wayne E. King Nigel D. Browning
9:00	Strain Mapping with Aberration-Corrected HRTEM	Martin Hytch
9:30	Atomic-Scale Study of Oxide Ferroelectrics by High-Resolution Transmission Electron Microscopy	Chunlin Jia
10:00	Imaging and Exit Wave Reconstruction in an Aberration-Free Environment	Angus Kirkland
10:30	Coffee Break	
11:00	Disruptive Technologies and the Frontiers of Electron Microscopy	Christian Kisielowski
11:30	Atomic-Scale Studies of Complex Oxide Interfaces Using Aberration-Corrected Z-contrast Imaging and EELS	Robert Klie
12:00	Image Formation in High Resolution Scanning Transmission Electron Microscopy	Mark Oxley
12:30	Lunch — Upper Patio	

Monday PM - Interfaces

Manfred Ruehle and Michael Mills, Chairs

14:00	Composition and Atomic Structure at the Si-SiO ₂ Interface Under HfO ₂	Philip Batson
14:30	Atomic Resolution, Z-contrast and In-Situ Characterization of Ceramic Interfaces	Yuichi Ikuhara
15:00	Mapping Grain Boundary Potentials by Inline Electron Holography	Christoph Koch
15:30	Coffee Break	
16:00	Interfaces and Defects in Perovskite Heterostructures	David Muller
16:30	The Origin of Characteristic Grain Boundary Distributions in Polycrystalline Materials	Gregory Rohrer
17:00	Quantifying HAADF-STEM Contrast: Application to Interfaces	Susanne Stemmer

Monday Evening - Poster Session

Bryan Reed and John Silcox, Chairs

17:30	Reception, Poster Session — Chardonney Room
18:30	Dinner — Vineyard Room
20:00	Poster Session, Coffee — Chardonnay Room

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Sessions

Tuesday AM - Ultrafast & In-situ Electron Microscopy John Spence and Ian Robertson, Chairs

9:00	In-situ Studies of Martensitic Phase Transformations using the Dynamic Transmission Electron Microscope	Thomas LaGrange
9:30	Time Resolved Photoemission Microscopy	Frank Meyer zu Heringdorf
10:00	Femtosecond Electron Diffraction: Atomic-Level “Movies” of Condensed Phase Dynamics	Dwayne Miller
10:30	Coffee Break	
11:00	Ultrafast Electron Nano-Crystallography	Yoshie Murooka
11:30	Radio-Frequency electron pulse compression for near single-shot, sub-100 fs diffraction in the 100 keV range	Brad Siwick
12:00	Lunch — Vineyard Room	

Tuesday PM - 3-D Imaging and FIB Paul Midgley and Michael Miller, Chairs

14:00	3D Materials Characterization using aberration-corrected STEM	Klaus Van Benthem
14:30	Optimal imaging conditions for electron tomography of inorganic materials	Matthew Weyland
15:00	3D orientation microscopy by combined FIB-serial sectioning EBSD-based orientation microscopy: principles and applications	Stefan Zaefferer
15:30	Coffee Break	

Holography – Rafal Dunin-Borkowski, Chair

16:00	Holographic tomography for quantitative dopant profiling	Alison Harrison
16:30	Challenges beyond Atomic Structure tackled by Electron Holography	Michael Lehmann
17:00	Unavailable	Molly McCartney
17:30	Reception — Upper Patio	
18:15	Dinner — Vineyard Room	

Sessions

Wednesday AM - Ultrafast & In-situ Electron Microscopy John Spence and Ian Robertson, Chairs

9:00	Mechanisms of Dislocation-Particle Bypass in Al Alloys Revealed using In-Situ TEM Deformation Experiments	Blythe Clark
9:30	In Situ Environmental TEM Studies of Cerium-Based Oxides	Peter Crozier
10:00	In-situ TEM studies of magnetisation reversal and transport in magnetic nanostructures	Amanda Petford Long
10:30	Coffee Break	
11:00	Nano-compression testing inside a TEM	Andrew Minor
11:30	Nucleation and growth kinetics of semiconductor nanowires	Frances Ross
12:00	Using Real Time Electron Microscopy to Understand Nucleation and Growth in Semiconducting Nanowires and Carbon Nanotubes	Eric Stach

Wednesday PM - Free Afternoon

Sessions

Thursday AM - 3-D Imaging and FIB Paul Midgley and Michael Miller, Chairs

9:00	The 3-D Morphology and Electronic Structure of GaN-Based Nanowires	Ilke Arslan
9:30	FIB-Based Techniques for 3D Imaging	Lucille Giannuzzi
10:00	Understanding Atom Probe Evaporation in Alloys and Semiconductors using Cross-Correlative TEM	Brian Gorman
10:30	Coffee Break	
11 :00	Geometrical Aspects of Polymer Morphologies Studied by Electron Tomography	Hiroshi Jinnai
11 :30	Equilibration of clusters: Ag in Al	Emmanuelle Marquis
12:00	Three Dimensional Analysis of Semiconductor Device Structures using LEAP	Sam Moore
12:30	Lunch — Vineyard Room	

Thursday PM - Intersection of Biology & Materials Mehmet Sarikaya and Juergen Plitzko, Chairs

14:00	Cryo-EM of Biological Nano-Machine and Cell	Wah Chiu
14:30	Low-dose aberration corrected cryo-electron microscopy of organic/biological specimens	Henning Stahlberg
15:00	Needs for Next-Generation EM Instrumentation in Structural Biology	Mike Marko
15:30	“Time resolved” 3 dimensional cryo-TEM to study CaCO ₃ crystallization on an self-organized organic template	Nico Sommerdijk
16:00	Coffee Break	
16:45	Distinguished Lecture and Reception: “Fifty Years Old and Still Going Strong”	Professor L. Michael Brown FRS

Thursday Evening

20:00	Reception — Upper Lobby
20:45	Conference Dinner — Vineyard Room

Sessions

Friday AM - Analytical Electron Microscopy

Joachim Mayer and Yimei Zhu, Chairs

9:00	Deformations in Carbon Nanotubes and Metal Nanoparticles: Results from Modeling Coherent Nanoarea Electron Diffraction Patterns	Jian-Min Zuo
9:30	Recent development of soft-X-ray emission spectroscopy instruments for a conventional analytical transmission electron microscope	Masami Terauchi
10:00	Electron Energy-Loss Spectroscopy of Surface Excitations near Interband Transitions in Nanomaterials	Cheng. Hsuan. Chen
10:30	Coffee Break	
11:00	Mapping electron excitations in the visible-UV range using sub-nm resolved STEM-EELS spectrum imaging	Mathieu Kociak
11:30	Electron Energy-Loss and X-ray Spectrum Imaging for Materials Characterization in Aberration-Corrected Scanning Transmission Electron Microscopes	Masashi Watanabe
12:00	Applications, Limits and Prospects of Valence Electron Energy-Loss Spectroscopy in Transmission Electron Microscopy	Rolf Erni

Strain Mapping with Aberration-Corrected HRTEM

Martin Hÿtch, Florian Hÿe, Florent Houdellier, Alain Claverie and Etienne Snoeck

CEMES-CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France, E-mail: hytch@cemes.fr

We will present the current state of the art in strain mapping at the nanoscale by a combination of high-resolution electron microscopy (HRTEM) and geometric phase analysis (GPA). Under favorable conditions, two-dimensional strain tensors can be measured to an accuracy of 0.1% across relatively large areas of specimen (100s nm) with nanometer spatial resolution. The different steps of the process will be described, including calibrations and optimum experimental conditions. For example, we will show how geometric distortions from the microscope lenses and detector system can be calibrated and removed. Finite-element modeling (FEM) coupled with full atomistic image simulations taking into account the 3-dimensional strain distribution can be used to address the problem of relaxation of the thin samples used for microscopy observations. We will show the considerable advantages that can be obtained by using microscopes equipped with imaging aberration correctors, such as the SACTEM-Toulouse, and preparing samples with focused ion beams (FIB). Examples will be given from studies of nanosystems for which strain is particularly important, such as semiconductor thin films, MOSFET transistors using strained-silicon technology, and strained nanocrystals.

Atomic-Scale Study of Oxide Ferroelectrics by High-Resolution Transmission Electron Microscopy

C.L. Jia and K. Urban

Institute of Solid State Research and Ernst Ruska Centre for Microscopy
and Spectroscopy with Electrons, Research Centre Jülich, D-52425 Jülich, Germany
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Thin epitaxial films of ferroelectric oxides, such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and BaTiO_3 , have attracted considerable attention with respect to potential applications in nanoelectronic high-density memory devices. The chief problem in the device applications is the achievable magnitude and stability of the switchable ferroelectric polarization of the thin films. Since ferroelectricity is strongly influenced by surfaces, interfaces and domain boundaries there is great interest in understanding how the local atomic structure affects the electric properties.

By means of high-resolution transmission electron microscopy the local polarization of thin $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films is studied on an atomic scale. The relative displacements of ions in unit cells are measured employing a technique of image mapping combined with detailed structure modelling and computer-based quantum mechanical image calculations. On the basis of the measured displacements of ions the local spontaneous polarization is calculated. It is found that the interfaces, surfaces and lattice defects have strong effect on the local spontaneous polarization. A systematic reduction of the atomic displacements and thus the polarization is measured at the interfaces and at the film surface. This suggests that interface-induced intrinsic suppression of the ferroelectric polarization plays a critical role in the size effect of nanoscale ferroelectrics.

Imaging and Exit Wave Reconstruction in an Aberration-Free Environment

A. I. Kirkland, Lan-Yun Chang, S. Haigh and C. J. D. Hetherington

Department of Materials, Parks Road, Oxford, OX1 3PH, UK

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Electron-Optical aberration correctors are now firmly established as a key component in many commercial Transmission and Scanning Transmission Electron Microscopes installed around the world. Equally, algorithms that recover the complex specimen exit plane wavefunction from a series of images recorded using one of several possible experimental geometries have also advanced to the point where several commercial software implementations utilizing this approach are readily available.

This paper will discuss the combination of these two complementary approaches with particular reference to exit wave reconstruction from a series of tilted illumination images recorded for several azimuths. This latter geometry benefits substantially from initial electron optical aberration correction which enables larger tilt angles to be used during data acquisition. Direct correction of the spherical aberration also relaxes the otherwise stringent relationship that conditions the defocus and illumination tilt. I will discuss recent calculations that define optimal conditions for tilt azimuth based reconstructions with reference to the effects of higher order aberrations beyond those that can be corrected directly as well as the effects of finite chromatic aberration and sample thickness. It will be shown that overall these effects combine to allow optimal tilt angles of up to ca. 17mrad to be used (at 200kV) compared to ca. 4mrad in uncorrected instruments with a consequent improvement in the resolution of the reconstructed data.

In addition to the above theoretical considerations exit wave reconstruction under aberration corrected conditions also places stringent requirements on instrumental stability. We have recently installed our second generation double corrected 200kV instrument (JEOL JEM 2200MCO) in Oxford. This microscope incorporates both imaging and probe forming aberration correctors in addition to a number of design improvements leading to increased stability. Initial data from this machine will be presented demonstrating axial information transfer at $<0.8\text{nm}$ in TEM.

Disruptive Technologies and the Frontiers of Electron Microscopy

Christian Kisielowski

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A disruptive technology is a technological innovation that eventually overturns the existing dominant technology or status quo product in a market. For example, the introduction of aberration correctors for electron microscopes and their further development in DoE's TEAM Project [1] overturn the traditional limits to resolution in electron microscopy or the Helios Project at LBNL [2] aims at more sustainable solutions to the global energy consumption by exploring cost efficient alternatives for harvesting solar energy that could overturn current technologies. In fact, many of the past advancements in electron microscopy base on the introduction of disruptive technologies and the versatility of the strong scattering of electrons in solids make electron microscopy a primary research tool that is steadily improved.

On the other hand there are notorious deficits linked to the application of transmission electron microscopy. Two of them are the preparation of electron transparent samples and a traditional distinction between electron microscopy of soft and hard materials that resulted in the development of distinctly different experiments. Since long these drawbacks are well known. Possible solutions, however, need yet to be found. With the recent improvements of instrumentation it is timely and necessary to revisit these drawbacks since electron tomography with atomic resolution is certainly limited by sample preparation and the rapid development of composite materials calls for a simultaneous recording of hard and soft materials and their interfaces. This contribution describes disruptive technologies that are currently explored to address both issues.

The importance of sample preparation is discussed in relation to an ongoing debate about the indium distribution in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys [3]. It will be shown that existing differences relate primarily to sample preparation and that the atomic distribution of indium atoms in alloys with $x < 0.2$ is currently poorly known. Improvements in sample preparation techniques and instrumentation, however, have progressed to a point where an investigation of cluster formation in solids becomes feasible. Moreover, it is shown that a combination of phase plate technology [4] and aberration correction allows for the introduction of a new imaging mode with $\text{Cs}=\Delta f=0$ and with a minimal loss of resolution if Cc correction is employed. As a result direct image processing can be executed to recover amplitude and phase of the electron exit wave function from 2 images only. Thereby, interfaces between soft and hard materials can be imaged simultaneously in an optimized fashion.

References:

- [1] <http://www.lbl.gov/LBLPrograms/TEAM/index.html>
- [2] http://www.lbl.gov/msd/helios_site/index_helios.html
- [3] Bartel, T.P., et al., Phase separation in $\text{In}_x\text{Ga}_{1-x}\text{N}$. Philosophical Magazine, 2007. **87**(13): p. 1983 – 1998
- [4] W.K. Hsieh, et al. Contrast Transfer Function Design by an Electrostatic Phase Plate, Microscopy and Microanalysis, 2007

Atomic-Scale Studies of Complex Oxide Interfaces Using Aberration-Corrected Z-contrast Imaging and EELS

R.F. Klie, Y. Zhao, G. Yang

Department of Physics, University of Illinois at Chicago, 845 W Taylor Street, M/C 273,
Chicago, IL 60607

Interfaces in complex oxide materials have been an enduring theme in materials physics, where the interplay of the reduced dimensionality, proximity effects, and surface relaxation and reconstruction creates interfacial states that are distinct from their bulk counterparts. It has been recognized that the perovskite oxides provide a unique opportunity to bring materials with diverse and mutually exclusive properties into intimate contact, and create interfaces with excellent structural and chemical compatibility and potentially novel properties.

In this presentation, aberration-corrected Z-contrast imaging and EELS in combination with in-situ heating/cooling experiments of interfaces in perovskite-type oxides will be shown. More specifically, we utilize the aberration-corrected JEOL2100FS at Brookhaven National Laboratory, the aberration-corrected VG HB-601UX at UIC and the conventional JEOL2010F TEM/STEM for our experiments in the temperature range between 10 K and 700 K. We will discuss our recent results, including the role of oxygen vacancies in the ultrathin SrTiO₃/GaAs hetero-interface, the effect of the spin-state transition of the Co³⁺ ions in LaCoO₃, and the effects of charge transfer in the Ca₃Co₄O₉.

The ultrathin SrTiO₃/GaAs interface consists of five monolayers of SrTiO₃(001) on GaAs (110), which are shown to be atomically flat without any obvious surface reconstruction and no significant diffusion between the film and the substrate.¹ While the SrTiO₃ film is highly oxygen deficient, the Fermi-level remains unpinned at the interface after a Ti-prelayer deposition.² Our ab-initio DFT calculation suggest that O-vacancies at the hetero-interface compensate the dangling bonds from the unreconstructed As-terminated GaAs (110) surface, and therefore play an important role in engineering the interfacial properties of this novel high-k dielectric. Our temperature study of LaCoO₃ shows the effect of the Co³⁺-ion spin-state transition, which occurs at T_s~90K, on the fine-structure of the O K-edge. While the crystal structure of LaCoO₃ does not change during the in-situ cooling experiment to 10K, the O K-edge pre-peak intensity decreases for T>T_s. A detailed analysis of the O K-edge fine-structure and comparative DFT calculations will be presented.³

The misfit-layered structure Ca₃Co₄O₉, consists of triple rock salt-type layers Ca₂CoO₃ and single CdI₂-type CoO₂-layers stacked along the c-axis.⁴ We will present aberration-corrected Z-contrast imaging and atomic-column resolved EELS in conjunction with multiple scattering calculations to elucidate the effects of charge transfer between the different Co-layers and its effect on the thermoelectric properties of Ca₃Co₄O₉. Detailed analysis of this structure and the effects of in-situ heating and cooling on the Co-valence and spin-state will be discussed.

References:

¹ R. F. Klie, Y. Zhu, E. I. Altman, et al., Applied Physics Letters **87** (2005).

² Y. Liang, J. Curless, and D. McCready, Applied Physics Letters **86** (2005).

³ R. F. Klie, J. C. Zheng, Y. Zhu, et al., Phys. Rev. Lett. (submitted) (2006).

⁴ A. C. Masset, C. Michel, A. Maignan, et al., Physical Review B **62**, 166 (2000).

Image Formation in High Resolution Scanning Transmission Electron Microscopy

Mark P. Oxley and Stephen J. Pennycook

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Scanning transmission electron microscopy (STEM) offers many imaging modes based on both elastic and inelastic scattering of the incident electron probe. These can be used to gain complementary information about a sample and also provide insights into the image formation processes responsible for each type of image. For example, the electrons scattered through large angles into an annular dark field detector cannot also be scattered into a bright field detector. Electron energy loss spectroscopy (EELS) provides information about electrons that have undergone a range of energy losses. The elastically scattered and thermal diffuse scattered electrons form the zero loss peak (ZLP). The ZLP can be used to provide insight into the formation of images based on low-loss and core-loss events, the so called “preservation of contrast”.

In this presentation we will examine the processes contributing to the formation of atomic resolution images in the STEM. In particular we will examine image localization and contrast and the requirements for maximizing each. The relationship between images formed by core-loss EELS and ZLP will also be examined.

This research was sponsored by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U.S. Department of Energy and by appointment (MPO) to the ORNL Postdoctoral Research Program administered jointly by ORNL and ORISE and by the ORNL Laboratory Directed Research and Development Program.

Composition and Atomic Structure at the Si-SiO₂ Interface Under HfO₂

P.E. Batson

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Device quality hi-K gate dielectric structures are often accompanied by growth of a layer of SiO₂ between deposited HfO₂ or HfSiO₄ and the underlying Si substrate. This layer can be relatively thick if formed by decomposition of the Hf silicate at high temperature, or it can be very thin for direct HfO₂ deposition. HAADF imaging results for the Si-SiO₂ interface using the IBM sub-Å STEM show interesting structural units which are evidence for interface reconstruction involving oxygen or silicon, and which influence the amount of stress in the Si and oxide. Imaging also shows dynamically changing contrast that is likely caused by the presence of isolated Hf atoms, moving within the oxide under the electron beam. Electron Energy Loss Spectroscopy, using a non-local analysis of Hf scattering in the low loss region, confirms the presence of Hf within the oxide.

Atomic Resolution, Z-contrast and In-Situ Characterization of Ceramic Interfaces

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Interfaces in ceramics play an important role on the various properties. It has been known that the addition of small amount of dopants strongly improve the mechanical and functional properties in polycrystalline ceramics. Z-contrast images obtained by scanning transmission electron microscopy (STEM) is powerful technique to experimentally determine the location of the dopants segregated at grain boundaries. As the image intensity in the Z-contrast is approximately proportional to the square of the atomic number, STEM technique is especially well suited for understanding the role of heavy impurities in grain boundaries composed of much lighter ions. In this study, the well-defined grain boundaries in Al_2O_3 and ZnO bicrystals doped with Y and Pr were observed by using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Cs-corrected-STEM was used for the present experiments (Cs-corrector attached JEM-2100F, JEOL Co. Ltd.), and the HAADF detector with an inner angle greater than 60 mrad. was used with an probe size about 0.1nm.

In the Z-contrast image of the Y-doped $\Sigma 31$ grain boundary in Al_2O_3 , bright columns that lie periodically along the boundary plane were observed, indicating the presence of Y at specific sites [1]. According to the first principles calculations, the presence of Y at the 7-membered rings was found to increase the number of bonds, and the bond strength was increased due to the higher covalency of the Y-O bonds. This should result in a much stronger grain boundary, which explains why the Y-doped grain boundaries can have such a large increase to creep resistance despite the fact that only a small amount of Y is present. In the Z-contrast image of the Pr-doped ZnO $\Sigma 7$ boundaries, bright spots were also periodically found along the GB [2]. Since the atomic number of Pr is larger than that of Zn, the bright spots correspond to the presence of Pr. The Pr is only found at the specific atomic columns of the boundary plane, that is, the Pr segregates to the specific atomic sites of the boundary. The most stable atomic grain boundary structure calculated by the first-principles calculations was basically similar to that is deduced from the Z-contrast image. It was found that the origin of the varistor properties is due to the formation of Zn vacancies which were generated by the Pr segregation. Furthermore, BF-STEM technique can be applied to directly observe light elements in ceramics. An example to discriminate oxygen and aluminum atoms in the dislocation core in alumina will be shown in the presentation [3].

References:

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Mapping Grain Boundary Potentials by Inline Electron Holography

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A thorough characterization of materials, such as ceramics, whose properties are controlled by internal interfaces includes the characterization of individual interfaces within the material. Transmission electron microscopy is an excellent tool for investigating structure and composition of such internal interfaces at very high resolution. Recently off-axis electron holography has been used for mapping potential profiles across grain boundaries in ceramic materials. Profiles of the projected inner potential across interfaces give insight into segregation and accumulation and extent of space charge.

The phase of an electron wave passing through a specimen can only be measured by interfering it with a reference wave (off-axis holography) or itself (inline holography). Some of the advantages of inline holography over off-axis holography are: (a) very simple experimental setup (works in any TEM), (b) may record holograms far away from specimen edge, and (c) specimen drift may easily be compensated. The disadvantage: complicated non-linear equations have to be solved for reconstructing the complex electron wave function, while off-axis holography is linear. Focal series reconstruction algorithms available in the literature use an approximation to the image formation equation which reduces flux with defocus. This is unphysical and works therefore only for small defocus. We will report on first experimental results obtained with a flux-preserving inline holography reconstruction algorithm [1] which allows the reconstruction of focal series recorded over a large focal range.

Up to the limits defined by the spatial incoherence, given a certain size of the objective aperture the distance between points in the electron wave function whose relative phase difference may contribute to the image intensity is proportional to the defocus under which the image has been recorded. This means that very large defoci are necessary for recovering very low spatial frequency components of the complex exit face electron wave function. In a real microscope, images with such large differences in defocus differ also in magnification, image rotation, and possibly other distortions and aberrations.

We will report on the recent development of a software tool for the automated reconstruction of maps of the electron wave phase shift from general experimental focal series of TEM images, taking changes in image rotation and magnification into account. This method has been applied to the determination of potential profiles across interfaces in various ceramics.

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Interfaces and Defects in Perovskite Heterostructures

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Electron energy loss spectroscopy (EELS) provides direct information on the local electronic structure of a material at the atomic scale. In ionic systems, EELS measurements of oxygen vacancies and cation formal valences give insight and place remarkable constraints on the structure and stability of heterointerfaces and defects. This is of considerable importance to the field of oxide electronics and ferroelectrics, where the growth of atomically-abrupt heterointerfaces has been a central goal. However, when the interfaces are between polar and nonpolar layers, electrical and atomic abruptness turn out to be mutually incompatible goals. This is the bulk analogy of the surface reconstructions found in polar systems where a material terminated along a bulk polar plane has a net charge and a divergent surface energy. The mechanisms by which compensating charges can be introduced are varied and sensitive to growth and substrate conditions, ranging from electronic reconstructions in mixed valence systems to changes in interface stoichiometry and the creations of defects such as oxygen vacancies. This is illustrated for interfaces between SrTiO_3 and LaAlO_3 , LaTiO_3 and other related systems such as Vanadates.

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The Origin of Characteristic Grain Boundary Distributions in Polycrystalline Materials

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It is widely recognized that the types of grain boundaries in a material and the manner in which they are connected affect a wide range of properties and, ultimately, a material's performance and lifetime. Understanding causal structure/property relationships relies on accurate descriptions of the grain boundary network, which is structurally complex. To distinguish one grain boundary from another, it is necessary to characterize five independent parameters. Furthermore, the different types of grain boundaries are connected in non-random configurations. To capture this complexity, we have developed techniques to measure the five-dimensional grain boundary character distribution (the relative areas of different boundary types, distinguished by lattice misorientation and grain boundary plane orientation). Based on observations in a range of metals and ceramics (Al, grain boundary engineered Ni, Cu, and α -brass, Fe-1%Si, WC, MgO, SrTiO₃, TiO₂, MgAl₂O₄, and Al₂O₃), we are beginning to understand how the grain boundary character distribution evolves with time and is influenced by impurities and processing conditions. One general observation that will be described in this talk is that grains within polycrystals have preferred habit planes that correspond to the same low energy, low index planes that dominate the external growth forms and equilibrium shapes of isolated crystals of the same phase. A second topic will be the probable existence of a steady state grain boundary character distribution that is correlated to grain boundary energies and is established in the early stages of growth. A theory for the development of steady state, characteristic grain boundary character distributions will be described.

Quantifying HAADF-STEM Contrast: Application to Interfaces

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High-angle annular dark field (HAADF) imaging in scanning transmission electron microscopy (STEM) provides chemically sensitive atomic resolution structure images that are generally more directly interpretable than conventional high-resolution transmission electron microscopy images. This presentation will focus on the quantitative interpretation of HAADF image contrast in terms of the occupancy of atomic columns for determining the atomic structure and chemistry of interfaces.

In the first part of the presentation we discuss the influence of sample thickness and defocus on HAADF image contrast for a wide range of materials with different crystal structures, lattice spacings and atomic numbers. These model crystals included the perovskites PbTiO_3 and SrTiO_3 , zinc blende InP and InGaAs , as well as silicon. The latter material was also imaged along different crystallographic directions to investigate the influence of lattice spacings on HAADF contrast. Atom column intensities are compared in experiments and image simulations, which were obtained using different theoretical approaches. The intensity of a background, measured between the columns, is also evaluated and found to be correlated with the average atomic number in the crystals. In silicon, the background was largely independent of the column spacing. The contrast was lower in the experiments than in the simulations. We discuss whether this follows because the background is higher in the experiments or whether simple simulations overestimate the contrast because spatial incoherence and instabilities are not taken into account. We show that for silicon relatively good match between simulations and experiments can be achieved by considering the latter. In materials containing elements of higher atomic numbers there are qualitative differences between simulations and experiments, both in the relative intensities and the behavior of contrast as a function of thickness. We explore the extent to which the comparison of experimental atom column intensities with image simulations is aided by subtraction of the background for this data. We also discuss the consequences for interface analysis where the background is less well defined and where atomic displacements may influence the contrast.

In-Situ Studies of Martensitic Phase Transformations Using the Dynamic Transmission Electron Microscope

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Martensitic transformations occur by a rapid lattice-distortive mechanism, where the kinetics and morphology of the transformation are dominated by the strain energy. Since no diffusion is involved in these transformations, phase fronts can move at velocities near the speed of sound. Thus, it has been difficult to characterize interface dynamics and nucleation events in martensites. Understanding these rapid events has many impacts on scientific and technical fronts. To meet the need for studying fast dynamics in material processes, we have constructed a nanosecond dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory to improve the temporal resolution of in-situ TEM observations.

The DTEM consists of a modified JEOL 2000FX transmission electron microscope that provides access for two pulsed laser beams. One laser drives the photocathode (which replaces the standard thermionic cathode) to produce the brief electron pulse. The other strikes the sample, initiating the process to be studied. A series of pump-probe experiments with varying time delays enable, for example, the reconstruction of the typical sequence of events occurring during the martensitic phase transformation.

This presentation will discuss investigations in two different alloy systems, Ti and NiTi alloys. The α to β transition in pure Ti at high heating rates (above 3000 K/s) occurs by an 'isothermal' type martensitic transformation which is rate dependent. The martensitic transformations in stoichiometric NiTi are characterized as 'athermal' types and are time independent, where the transformed fraction is proportional to the amount of undercooling or overheating. Using single-shot SAED and brightfield imaging, we have characterized the nucleation events and transformation behavior in these two materials and have made a qualitative comparison of their differences in kinetics.

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Time Resolved Photoemission Microscopy

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The decay of electronic excitations at surfaces and especially the overall lifetime of such excitations is typically studied in pump-probe experiments where a first (pump)-laser pulse is used to excite the electronic system and a second (probe)-laser pulse triggers photoemission from the excited state. Variation of the delay-time between pump- and probe- pulse then allows following the decay of the electronic excitation, averaged over the surface. The experimental data obtained in such integral experiments, however, can be difficult to interpret, especially for heterogeneous surfaces. To study the influence of the microscopic morphology of a surface on the lifetime of electronic excitations requires spatial resolution in addition to the pump-probe experiment.

We combined a Spectroscopic Photoemission Microscope (SPE-PEEM) and a femtosecond Ti:Sapphire Laser oscillator as illumination source to study the interaction of light with metallic particles, and to observe the propagation of the excitation in time and space. I will present an approach that utilizes self-organization of Ag on Si(001) to generate well-defined structures *in-situ* inside the microscope. If Ag is deposited at $T \sim 600^\circ\text{C}$ on vicinal Si(001) surfaces, quasi one-dimensional wires are formed alongside compact islands. Such structures will then be used to study their interaction with intense fs--laser pulses.

Femtosecond Electron Diffraction: Atomic-Level “Movies” of Condensed Phase Dynamics

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Femtosecond Electron Diffraction (FED) combines the high spatial resolving power of electron diffraction with the ultrafast time scales of optical spectroscopy in a single technique capable of capturing structural changes on the atomic scale in real time. At the core of FED technology is a pulsed electron source driven by photoemission with a femtosecond laser pulse and subsequent acceleration of electrons by a DC field. Since electron pulses broaden during propagation due to space charge, the temporal resolution of an FED experiment is mainly determined by the duration of the electron pulse at the sample position. We employ a compact gun design to deliver pulses as short as 200 fs in < 3 cm of propagation. These pulses have sufficient electron density to allow studies under non-reversible excitation conditions. The electron pulse duration was directly measured using the ponderomotive force of an intense laser pulse to sequentially scatter electrons [1]. Results of these measurements agree with N-body simulations performed with the Barnes-Hut Treecode algorithm [2].

We applied FED to study the structural response of thin free-standing metal and semiconductor films upon ultrafast photo-excitation within a wide range of excitation levels. These studies distinguish the different channels, thermal vs. non-thermal, of electronic energy relaxation resulting in different melting mechanisms for both classes of materials. We found that under highly driven excitations, relaxation in both Al [3] and Au [4] occurs via thermal mechanisms with equilibrium between electrons and lattice (and consequently melting) occurring on a ps time scale. However, Au exhibited a unique effect of bond hardening as indicated by an increased melting point at high electronic temperatures. This phenomenon of bond hardening agrees with *ab initio* simulations performed by Mazevet *et al.* [5]. In contrast to metals, we observed non-thermal collapse of the Si lattice in < 500 fs at excitation levels corresponding to more than 6% of the valence electrons [6]. These much faster dynamics indicate that the process is electronic in nature, i.e. the lattice collapse is attributed to a modification of the inter-atomic potential due to the promotion of a large density of valence (bonding) electrons to the conduction (anti-bonding) band. These and related systems will be discussed to give an overview of the fundamental differences in bonding in different classes of materials.

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Ultrafast Electron Nano-Crystallography

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The correlation between material structures and size-dependent properties is a fundamental problem in nanoscience. Through the development of ultrafast electron nano-crystallography, we have studied some important mechanisms pertaining to the nanometer scales.

To investigate the change in the phase transforming behavior from the bulk to the molecular length scale, we size-select and deposit nanoparticles (Au, Ag) on an interface using linker molecules as a buffer layer. Because the particles are sufficiently isolated from each other and from the substrate, a clear diffraction pattern can be obtained to yield the full-scale radial distribution function for particles as small as 2nm. This radial distribution function method allows the identification of changes of bonds in the system where a long-range order does not exist, a norm during structural transformation and for particles whose structures significantly modified by the interface. This is in contrast to examining the integrity of the Bragg peak, whose time-evolution reflects the average change experienced by the lattice as a whole. By following the changes in bond densities as a function of applied fluence, we identify a surface melting behavior that appears at 70% of the fluence for melting. Since we are able to survey the energy landscape by applying fluence below or above the melting threshold, the quasi-melting behavior can be examined, which is evidenced by the liquid residence time increasing with the applied fluence for 20 nm nanoparticles. Such distinguishable solid-liquid transition, however, does not exist for 2nm nanoparticles, as we cannot find a sharp transition between solid and liquid in their temporal evolutions. These contrasting behaviors reflect the first and second order phase transitions in small particles.

To explore the effects of electronic excitation on electron-lattice interactions and carrier dynamics in nanocarbon materials, we study 2-dimensional graphite and 1-dimensional carbon nanotube. Using field-dependent Bragg scattering, the femtosecond electronically driven lattice contraction is isolated from their intrinsic thermal behaviors following carrier recombination. The low-dimensional carrier diffusion is linked to the formation of interlayer bonds and the creation of a surface dipolar layer following optical electron-hole excitation. These phenomena are characteristic of the nanometer length scale, and their elucidations highlight the use of the ultrafast nanodiffraction methodology. In extension, we also examine the ultrafast molecular electronic properties by following both carrier and molecular structural responses on a self-assembled molecular electronic interface.

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Radio-Frequency Electron Pulse Compression for near Single-Shot, Sub-100 fs Diffraction in the 100 keV Range

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A novel method for producing sub-100 fs electron pulses, suitable for near single-shot ultrafast electron diffraction experiments in the 100 keV range, will be discussed. A combination of analytical estimates and state-of-the-art particle tracking simulations show that it is possible to create 100 keV, 0.1 pC, 30 fs electron bunches using relatively well-established electron beam techniques. Specifically, this new source is based on an initial stage of space-charge (Coulomb repulsion) driven pulse expansion – always present in ultrashort photoelectron pulses – that provides the energy-correlated electron bunches required for subsequent radio-frequency pulse compression in a second stage. This method does not try to *circumvent* the space-charge problem, the much discussed bogey-man of the field, but instead *makes use* of these space-charge induced bunch dynamics. In addition to a dramatic increase in time-resolution and pulse fluence, beam collimation is also significantly improved with this approach. I will discuss the limitations of this approach and show that they come from quite an unexpected source; the properties of the photoemission.

3D Materials Characterization Using Aberration-Corrected STEM

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Third-order aberration correction in scanning transmission electron microscopy (STEM) enables the characterization of materials with unprecedented detail by providing electron probe sizes smaller than 1 Ångström and single atom sensitivity. In the absence of significant lens aberrations, the probe-forming aperture can be increased in size. In addition to decreasing the lateral size of the probe, the increased probe-forming aperture leads to a significant reduction in the probe's depth of field. Consequently increased depth sensitivity is achieved. By through-focal series acquisition of annular dark field images, the incoherent imaging conditions enable optical sectioning of the TEM sample similar to confocal optical microscopy.

In the presentation we will illustrate the feasibility of this new imaging technique, discuss vertical spatial resolution limits and limitations, and show several examples obtained from different materials systems. The vertical resolution and sensitivity can be enhanced by a differential image processing techniques, image filtering and deconvolution algorithms. First results will be reviewed and discussed.

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Optimal Imaging Conditions for Electron Tomography of Inorganic Materials

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Electron tomography has emerged in recent years as arguably the most powerful structural characterization tool available to the nano-engineer. This emergence, its foundations rooted in the biological application of the technique, has been driven by the need to characterize the diverse three dimensional nanostructures generated by both bottom-up and top-down approaches. While both biological and non-biological systems need to be characterized on similar length scales the optimal technique(s) for such analysis are largely dissimilar. The principal challenge to the physical scientist in applying electron tomography is the range of materials from which nano-structures are built; these range from polymeric materials to ceramics and everything imaginable in-between. This is in stark contrast to the biological application of electron tomography, where the material under study is largely proteinaceous material. There are two central factors to carrying out electron tomography; maximizing the contrast of structural features above the noise level and avoiding damage during acquisition. While bright field (BF) TEM is clearly the technique of choice for frozen hydrated biological material, where phase contrast gives greater contrast than any other suitable technique, this will clearly not be the case for most materials systems. Indeed for many materials systems, which are typically well away from any weak phase approximation, phase contrast is probably the least suitable technique. However the physical sciences have a long history of applying a diverse range electron microscopy modes and imaging techniques; many of which are more suitable to tomography than classical BF TEM. However this diversity of techniques leads to much less certainty about the most suitable approach for any particular material. In order to illustrate the diverse approach required to electron tomography of inorganic materials case studies are demonstrated in applying the technique. These include the analysis of nanoscale precipitates in model Aluminium aerospace alloys by high angle annular dark field (HAADF) scanning transmission electron (STEM) tomography, the morphological analysis of silicon quantum dots in silica by plasmon tomography and the characterization of thick, high atomic number, materials by incoherent bright field (IBF) STEM tomography. In each case the approach to optimizing the conditions of the acquisition in terms of contrast, beam damage and signal to noise ratios will be described. Finally the implications of a new generation of aberration corrected instruments for the future of electron tomography will be discussed.

3D Orientation Microscopy by Combined FIB-Serial Sectioning EBSD-Based Orientation Microscopy: Principles and Applications

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In the present work we report our recent progress in development and optimization of a technique for the 3-dimensional high resolution characterization of crystalline microstructures. The technique is based on fully automated serial sectioning using a focused ion beam (FIB) and characterization of the sections by orientation microscopy based on electron backscatter diffraction (EBSD) in a combined FIB-scanning electron microscope (SEM). On our system, consisting of a Zeiss Crossbeam FIB-SEM and a TSL/EDAX EBSD system the technique currently reaches a spatial resolution of $100 \times 100 \times 100 \text{ nm}^3$ as a standard, but a resolution of $50 \times 50 \times 50 \text{ nm}^3$ seems to be a realistic optimum. The maximum observable volume is in the order of $50 \times 50 \times 50 \text{ }\mu\text{m}^3$.

Currently, two competing geometrical set-ups for the technique are available: on our system the EBSD camera is position opposite to the FIB column. As a consequence, sample movement between the sectioning and the EBSD position consists of a tilt and a y-movement of the stage only. This allows very precise sample positioning and flexible milling and measuring strategies. Alternatively, the EBSD camera may be positioned below the FIB column which requires, if a properly pre-tilted sample is used, a 180° rotation of the stage and minor corrections for the x- and y-position. A part of the presentation deals with the comparison of the two techniques.

The 3D orientation microscopy technique conserves all the powerful features of 2-dimensional EBSD-based orientation microscopy and extends them into the third dimension of space. This allows new parameters about the microstructure to be obtained, for example the full crystallographic characterization of all kinds of interfaces, including the morphology and the crystallographic indices of the interface planes.

The technique has been applied, up to now, to study a variety of different materials, including pearlite colonies in a carbon steel, twins in pseudo-nanocrystalline NiCo thin films, deformation patterns formed under nano-indents in copper single crystals and fatigue cracks in an aluminum alloy. Also the 3-dimensional structure of nuclei of recrystallisation in heavily deformed Fe 36 % Ni has been studied.

It turned out that the technique is particularly suited to study microstructures with feature sizes (e.g. grain or subgrain sizes) in the order of few 100 nm to about 10 μm . In particular it is well suited to study even heavily deformed microstructures. Many metallic materials are accessible by the technique but there are few cases where important artefacts are created. Difficulties turn out, for example, when working with metastable austenitic structures which transform, under the action of the ion beam, into martensite. Also deformed aluminium is difficult to prepare because Ga and Al form a low-temperature melting eutectic at the grain boundaries. Finally, some intermetallic materials amorphise so deeply during milling that no EBSD patterns can be obtained.

Holographic Tomography for Quantitative Dopant Profiling

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Dopant profiling of semiconductor devices using off-axis electron holography has become more widely used in recent years, with many examples of the successful visualisation of dopant-related electrostatic potentials. Electrically biased holography experiments have also been carried out *in-situ* in the electron microscope in order to ensure that the device is examined under conditions that are as close to working conditions as possible [1]. Although electron holography promises to provide fully quantitative results, the measured potential is a two-dimensional projection along the electron beam direction through the semiconductor membrane thickness, thereby including all surface potential effects. These surface contributions are of particular interest when using electron holography to examine semiconductor device structures because focused ion beam (FIB) milling is required for site-specific membrane preparation of current generations of devices. This preparation technique is known to generate substantial amorphous and electrically altered surface layers. A three-dimensional characterisation of the electrostatic potential within a transmission electron microscope (TEM) membrane is required to reveal such surface effects, information which can be obtained through the use of electron tomography [2]. Electron tomography involves the use of a high angle tilt series of images to reconstruct three-dimensional information about a sample, and has previously been applied successfully to the examination of small particles such as catalysts.

Using a custom-built electrical biasing holder [3], electron tomography and electron holography experiments have been combined to investigate the three-dimensional potential distribution in semiconductor devices. A quantitative analysis of experimental results obtained from a range of device structures including MOSFETs and diodes revealed 3-D electrostatic potential variations arising from the presence of surfaces and damage generated by FIB sample preparation. Bulk-like properties are measured in the centre of the tomographic reconstruction of the specimen, revealing higher electrically active dopant concentrations compared to the measurements obtained at the specimen surfaces.

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Challenges beyond Atomic Structure Tackled by Electron Holography

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With introduction of TEMs, where the spherical aberration including all other third order aberrations of the objective lens can be corrected almost completely, structure determination with resolutions down to 0.07 nm is reported to be feasible. Furthermore, the signal piles up at atom positions due to aberration correction allowing even the imaging of oxygen atom columns. Consequently, the impression arises that the most difficult technical problems for atomic structure determination in TEM-imaging are solved; hence holographic methods like off-axis electron holography and focal series reconstruction might be considered obsolete, because their initial purpose of a-posteriori aberration correction is not needed anymore. However, the missing phase problem still persists preventing the measurement of pure phase objects like electric and magnetic fields, which determine the mesoscopic properties of most functional materials.

Consequently, holographic methods are more important than ever: Instabilities of TEM and corrector plus inaccurate measurements of aberrations during corrector alignment prevent recording atomic structures under controlled aberration conditions. Furthermore, deliberately introduced aberrations for Zernike phase contrast again cause non-negligible delocalization of object information in particular at non-periodic structures like e.g grain boundaries and interfaces. Eventually, long-ranging object properties like e.g. charge modulations and ferro- and piezoelectric polarizations are not registered in the conventional image intensity image. These difficulties become even more severe with better information limit of the TEM.

Therefore, combining Cs-correction with electron holography is more than ever an issue [1]. By means of electron holography, all residual coherent aberrations can be corrected yielding an information transfer from lowest spatial frequencies up to the information limit without transfer gaps. In particular, most interesting object information relevant for materials science can be found at low spatial frequencies. Ferroelectrics are a prominent example for demonstrating the importance of measurements beyond atomic structure imaging. In perovskite structures, the ferroelectric polarization is produced by a tetragonal distortion of the unit cell, giving rise to both the long-ranging ferroelectric polarizations [2] and the ferroelectric dipoles within unit cells. Also doped metal oxides have recently attracted attention due to the presence of intrinsic charge modulations, resulting in novel macroscopic properties. First holograms of $\text{In}_2\text{O}_3(\text{ZnO})_{m>6}$ have been recorded showing these space charge modulations and the resulting intrinsic electric fields [3]. For an accurate modeling of these findings, however, the only application of scattering factors for isolated atoms has become insufficient; these simulations have to be extended using the full electrostatic potential of crystals.

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Mechanisms of Dislocation-Particle Bypass in Al Alloys Revealed Using In-Situ TEM Deformation Experiments

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Particle-strengthened alloys are currently used throughout the aerospace and nuclear industries in applications ranging from airplane turbine blades to nuclear storage facilities. Although the behavior of these alloys is generally well-understood at room temperature, at elevated temperatures, such as those experienced during processing and in-service, the ability of dislocations to climb out of plane creates opportunity for more complex dislocation-particle interactions. Current creep models oversimplify these interactions, and as such are unable to accurately predict the creep behavior of particle-strengthened systems.

In this study, dislocation-particle interactions in Al-4Mg-0.3Sc and Al-0.3Sc were studied dynamically via elevated temperature, in-situ TEM straining experiments. In-situ observations between dislocations and semi-coherent Al₃Sc particles reveal a new high temperature bypass mechanism, involving a direct interaction between the dislocation and the particle-matrix interface, which gives rise to a detachment moment when the dislocation breaks free and re-enters the matrix. Observed interactions are seen to be much more complex and varied than previously considered. Whereas creep models generally consider only one dislocation character, one slip system, and a fixed plane of intersection, in-situ observations show dislocations of mixed character, approaching a given particle from multiple slip systems, and intersecting the particle at various locations depending on the geometry of slip. Additionally, dislocation interactions are seen to alter the interfacial structure of the particle, giving rise to an evolving microstructure as multiple dislocations interact with the same particle, and in turn affecting subsequent dislocation interactions. The system complexity is increased still by considering the effect of particle size and coherency on the nature of the interaction. Observations of interactions between dislocations and coherent Al₃Sc particles showed a transition to particle shearing as the dominant bypass mechanism for particles less than 12 nm, with operation of both mechanisms possible in the transition regime.

Collectively, these in-situ observations reveal new insight into the dislocation-particle bypass mechanisms occurring at elevated temperature. These new observations have the potential to improve the predictive capabilities of creep models. For example, a statistical probability could be used to describe the distribution of the various dislocation-particle interactions. Development of such physically-based models has implications for improving the prediction of material behavior in-service, as well as during processing.

***In Situ* Environmental TEM Studies of Cerium-Based Oxides**

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High surface area cerium-based oxides are important in catalytic and fuel cell applications because of their unique ability to reversibly form +3 and +4 valence oxides (CeO_2 and Ce_2O_3 respectively). The associated phase transformations are triggered by changes in the oxygen chemical potential allowing these materials to act as very effective oxygen buffers during oxidation and reduction reactions. Doping ceria with zirconium can substantially lower the temperature at which the phase transformations take place resulting in a more active catalyst. The activity of ceria zirconia depends not only on composition but also on the prior redox history. In particular, high temperature reduction treatments are found to favor the formation of highly active materials. However, there remain many questions about the role of compositional heterogeneity, cation ordering and oxygen vacancy ordering in the active component during redox. This is mainly because there is a strong thermodynamic driving force for Ce to exist in the +4 oxidation state at standard temperature and pressure making the active form of the material difficult to identify. For this reason, exploring of the active phases in cerium-based oxides must be carried out while varying the oxygen chemical potential. We have undertaken a detailed *in situ* transmission electron microscopy (TEM) study of the dynamic nanostructural and nanochemical changes that takes place in pure ceria and ceria zirconia during redox cycling.

High surface area samples were synthesized using wet chemical methods and characterized with X-ray diffraction and thermal gravimetric analysis. Direct atomic level observations of phase transformations taking place during redox in an H_2 rich atmosphere were carried out in a modified Tecnai F20 environmental transmission electron microscope. *In situ* high resolution imaging and electron diffraction were employed to monitor the changes in structure that took place during reduction and re-oxidation. Electron energy-loss spectroscopy was used to monitor the oxidation state of Ce during the redox process. *In situ* scanning transmission electron microscopy provided information on the correlation between composition and activity.

Experiments were conducted on pure ceria and ceria zirconia samples. The pure ceria samples showed clear evidence for oxygen vacancy ordering during reduction. The ceria zirconia samples were more active but also possessed a much more complex nanostructure showing both compositional variations and nanoscale regions with cation ordering. Many cation ordered regions appear to be inactive whereas regions with less cation ordering were active but did not show evidence for *oxygen* vacancy ordering during reduction.

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In-Situ TEM Studies of Magnetisation Reversal and Transport in Magnetic Nanostructures

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The rapid increase in information storage density, and in memory density and speed have been brought about in part by the development of new materials, often consisting of layered structures, with properties that are engineered by controlling their microstructure and chemical profile. The layer thicknesses are of the order of a few nanometres, and the films tend to be polycrystalline, resulting in variations in properties across the structures. One of the most spectacular examples is the development of devices based on the tunnel magnetoresistance (TMR) phenomenon, such as the spin-dependent tunnel junction used for read heads or magnetoresistive random access memories. In addition, single layer structures and bilayers are of importance for both media and memory applications, and because of fundamental interest in the behavior of magnetization structures such as magnetic vortices, which form to lower the total energy of the structure. The behavior of these materials relies on the local magnetic domain structure and magnetization reversal mechanism, and one of the techniques enabling micromagnetic studies at the sub-micron scale is Lorentz transmission electron microscopy (LTEM) which allows the magnetic domain structure and magnetization reversal mechanism of a FM material to be investigated dynamically in real-time with a resolution of a few nm. We have used LTEM and in-situ magnetizing experiments to make qualitative and quantitative studies of magnetization reversal in a range of materials including spin-tunnel junctions and patterned thin film elements. Quantitative analysis of the Lorentz TEM data has been carried out using the transport of intensity equation (TIE) approach. In addition to the local variations in the magnetic properties induced by the microstructure of the films, further variations arise when the films are patterned to form small elements and results will be presented for a range of structures patterned from single layers and bilayers and from device structures. The TMR phenomenon relies on spin-dependent tunneling across a nanoscale oxide barrier, and the structure and composition of the layer itself and of the interfaces with the ferromagnetic electrodes on either side is critical in controlling the transport behavior across the tunnel junction. Results will also be presented of tunneling measurements carried out in-situ in the TEM on cross-section samples, for which the nanostructure of the barrier at the exact position across which tunneling occurs can be imaged simultaneously with recording I-V curves. For example, the presence of asymmetry in the composition at the two interfaces leads to asymmetry in the tunneling behavior which can be observed from the in-situ measurements. The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science Laboratory, is operated under Contract No. DE-AC02-06CH11357.

Nano-Compression Testing Inside a TEM

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The technique of micro-pillar compression testing is quickly becoming a new paradigm for small-scale mechanical testing, particularly for examining size effects at small length scales. Through quantitative *in situ* nano-compression tests in a transmission electron microscope (TEM) we can directly correlate the dynamic deformation mechanisms in submicron pillars with simultaneous measurement of the imposed stresses. This talk will demonstrate this capability through the *in situ* compression of focused ion beam (FIB) machined metallic pillars with diameters between 150 and 400 nanometers. In pure Ni pillars we have found that the phenomenon of mechanical annealing leads to dislocation-free structures that allow for direct comparison of the deformation behavior across samples with dramatically different dislocation densities. In a second example we have systematically investigated two AA6063 alloys with identical compositions, one as-extruded and the other heat treated to increase the solute concentrations in the matrix. We found that the annealed sample exhibited a higher yield stress and greater deformability as compared to the as-extruded sample. Furthermore, our dynamic observations and comparison of the two alloys demonstrate that the dislocation plasticity behavior is quite different for the two samples. Our results will show that the nanoscale plasticity behavior seen during *in situ* deformation directly relates to the bulk ductility of these alloys. All of these results will be shown in relation to the size effects seen in *ex situ* pillar compression tests where a direct relation between the yield stress and the diameter of pillar structures has been confirmed.

Nucleation and Growth Kinetics of Semiconductor Nanowires

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The exciting applications of semiconductor nanowires can best be realised through a detailed understanding of their growth kinetics. For this it is important to quantify both the nucleation of wires from their catalyst particles and their subsequent steady-state growth. We have therefore examined both processes using time-resolved microscopy in a UHV-TEM. Si and Ge wires were grown from Au catalysts using chemical vapour deposition on flat Si surfaces, SiN substrates or pregrown III-V nanowire “stubs”. We firstly discuss a simple model for nucleation, which can explain the time at which nuclei first appear and their immediate growth rate. Subsequently, the variation of growth rate with pressure, temperature and droplet size allows us to determine the rate limiting steps for wire growth, while direct observations of the catalyst and wire structure show unexpected features of the growth process. We finally discuss the growth of nanowire heterostructures, in which the material supply is changed during growth. In situ observations of the nucleation of Si and Ge onto III-V nanowires suggest growth rules for predicting which materials combinations may be possible. Thus we find that in situ studies of nanowires provide a window into fundamental crystal growth processes, as well as an opportunity to fabricate precisely controlled structures for novel applications.

Using Real Time Electron Microscopy to Understand Nucleation and Growth in Semiconducting Nanowires and Carbon Nanotubes

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Semiconducting nanowires and carbon nanotubes are two of the primary 'new' materials of interest in the field of nanotechnology. This is because their small dimensions and unusual structures allow for new technologies to be established that exploit their unique electronic properties. We have been focused on understanding the mechanisms and kinetics associated with their nucleation and growth, in an attempt to provide a scientific framework for controlling their structure. Through the use of in-situ chemical vapor deposition in both ultra-high vacuum and at elevated pressures, we can observe the mechanisms of nucleation and quantitatively characterize the kinetics of these processes. In the case of vapor-liquid-solid silicon nanowire growth, we have found that the dissociative desorption of disilane is the rate limiting step. Additionally, after nucleation, we find that the nuclei undergo a rapid growth in size, driven by the supersaturation of silicon in the host gold-silicon liquid alloy drop. We will present a theoretical framework to describe this behavior which balances the roles of supersaturation, pressure and interface energies and show how this can be used to find the kinetic liquidus line in the AuSi phase diagram. In the case of carbon nanotube growth, we utilize a unique catalyst approach wherein the catalysts are firmly embedded in a silicon dioxide support film, so as to permit high resolution images of their surface structure at the onset of nanotube growth via the alcohol catalytic chemical vapor deposition process. We will report quantitative measurements of catalyst coarsening, and discuss how this process plays a controlling role in nanotube nucleation and subsequent growth. In each case, we will emphasize the power of the in-situ approach for providing quantitative data for discovering unique information regarding fundamental growth processes.

The 3-D Morphology and Electronic Structure of GaN-Based Nanowires

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Advances in nanotechnology have led to the demand and fabrication of smaller and smaller inorganic materials structures. One of the keys to successful device functionality is the ability to finely control the size, shape and electronic properties of the nanostructures. This requirement has most recently prompted the development of three-dimensional imaging on the nanoscale using scanning transmission electron microscope (STEM) tomography. Furthermore, as materials are being constrained to 0- and 1- dimensions and their surface to bulk ratio increases, the surface of the nanomaterial becomes increasingly important to its overall properties. The electronic structure of these surfaces can be studied with electron energy loss spectroscopy (EELS), and in particular, studying changes in the band gap in the low loss region of the spectrum.

Here we study GaN-based nanowires, which are important building blocks for a variety of different nanodevices, such as LEDs and lasers, transistors, and high mobility nanoelectronics. As a majority of nanowires in the literature are being grown by the cost-efficient and high yield vapor-liquid-solid (VLS) method, it is important to characterize and understand the properties of these nanowires, and their morphology with respect to the catalyst size, shape, and position on the nanowire. We have found the catalyst particle to be located in one of three positions at the tip of the nanowire, and we see that its properties affect the morphology of the nanowire. Furthermore, we have studied the electronic structure of two different surfaces of nanowires and see a different density of states for each, which we believe is correlated with the creation of surface states due to dangling bonds. These results will be presented and discussed. Work at Sandia is supported by the Department of Energy, under contract DE-AC04-94AL85000, and this research is partially funded by Sandia's President Harry S. Truman Fellowship in National Security Science and Engineering, a Laboratory Directed Research and Development Program (LDRD).

FIB-Based Techniques for 3D Imaging

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A focused ion beam (FIB) instrument allows for site specific sectioning of complex material systems. The signal detected at each FIB slice will depend on the type of 3D information that is acquired. The FIB itself can be used for modeling 3D microstructure by stacking multiple 2D FIB images obtained at sequential FIB slices. In addition to direct FIB imaging, one of the first uses of 3D FIB tomography was with analytical FIB/SIMS. Adding a scanning electron microscope (SEM) to a FIB to create a DualBeam instrument allows for FIB sectioning plus 3D information obtained via e.g., direct SEM SE or BSE imaging, SEM/EDS or SEM/EBSD signals. Advances in computer automation of the FIB slicing and subsequent signal detection has simplified the data acquisition process. The ultimate resolution of these techniques depends on the FIB slice thickness, which is a function of the ion-solid interactions for each target, and the spatial resolution of the signal detected at each FIB slice. Of course, FIB-based techniques can also be used to prepare specimens for other analytical instruments where 3D data can be obtained. Ubiquitous use of the FIB for the preparation of planar TEM specimens allows for (S)TEM tomography. More recently, FIB methods used to prepare cylindrical electron transparent specimens can be used for either on-axis (S)TEM tomography and/or for 3D atom probe. The advantage to on-axis (S)TEM tomography is that there is no missing information due to limitations in tilting planar specimens. Examples of FIB techniques for 3D imaging described above will be presented using a variety of different material systems.

Understanding Atom Probe Evaporation in Alloys and Semiconductors Using Cross-Correlative TEM

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Atomic level compositional and spatial characterization of metallic alloys and semiconductor devices are becoming essential in order to fully understand their electrical, optical, and even mechanical properties. The ability to accurately complete such characterization is being enhanced through improved electron optics as well as revisions to atom probe instrumentation. In order to take full advantage of the information attainable from atom probe tomography, several fundamental questions about the evaporation process need to be studied in detail. These include initial tip geometry formation processes under voltage and laser pulsing, tip shape evolution through interfaces of materials with different evaporation fields, field enhancement at conductor / dielectric interfaces leading to spurious evaporation away from the top surface, microstructure changes using laser pulsing, and failure mechanisms during evaporation. To answer these questions, we are currently cross-correlating atom probe tomography with ex-situ TEM before and after atom probe analysis. This talk will discuss our current state of hardware development enabling FIB preparation, TEM analysis of cylindrical geometries, and finally atom probe analysis on a single specimen. 1-D TEM and atom probe chemical correlation in recrystallized bulk metallic glasses illustrates that the tip geometry estimated from field enhancement calculations is correct within 5% of TEM measurements, but that oxide regions within recrystallized specimens can give incorrect reconstructions due to variations in evaporation field and dielectric constants. Pre- and post- atom probe analysis of Si-based specimens illustrates that laser pulsing can result in amorphization of the initially crystalline specimen and preferential evaporation from the “hot” side of the specimen. Laser pulsed atom probe analysis of Si-on-insulator specimens can lead to large microstructure changes including significant changes in tip aspect ratios and rounding of the specimen at interfaces. Since atom probe specimens are inherently electron transparent at TEM accelerating voltages, and also cylindrical, the possibilities for these specimens as theoretical tomography specimens are promising. Our efforts on TEM tomography of atom probe specimens and subsequent 3-D cross-correlation with atom probe data will be detailed. Finally, our efforts using the TEM tomography data for field modeling conductor / dielectric interfaces will also be detailed.

Geometrical Aspects of Polymer Morphologies Studied by Electron Tomography

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Recently, three-dimensional (3D) imaging of variety kinds of materials at nanometer scale becomes possible due to the progress of transmission electron microtomography (TEMT)[1]. In the TEMT experiments, a series of transmission electron micrographs from different tilt angles is taken, from which 3D structure(s) inside specimen is reconstructed. With careful sample preparation and alignment of the tilt series, the resolution of the 3D images approaches 1nm or less [2-3].

In materials science, it is essential to investigate the structure-property relationship of materials for better and accurate design of new materials. It is shown that new types of structural parameters that have never been acquired by other experimental techniques, e.g., scattering, conventional microscopy such as transmission electron microscopy, can be available from the 3D imaging. They are, for example, curvatures of interface [4], topology [5], shape, orientation and distribution of fillers [1,6] etc. In the present talk, we demonstrate how to measure some of these new structural parameters.

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Equilibration of Clusters: Ag in Al

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In the phase-separating Al-Ag system, intermediate metastable precipitates (Guinier Preston zones) are formed during aging of the supersaturated solid solution of Ag in Al. The metastable miscibility gap is characterized by a large asymmetry with a gap extending to 65 at.% Ag below 175°C and to 30-35 at.% Ag above 220°C. The exact structure of the GP zones (morphology, Ag concentration) is still matter of debate and the experimental studies published on this system have yet to concur. For instance, scattering experiments suggested two possible structures: an inverted shell structure with a Ag-rich core surrounded by an Al-rich shell, or a sphere of uniform Ag concentration [1]. Moreover, recent TEM observations have also indicated that in the initial stages of decomposition, GP zones could form with yet another morphology consisting of a Ag-rich shell surrounding an Al-rich inner core [2]. Clarifying the structural evolution in this model Al-Ag system is important to the understanding of alloys phase decompositions. This paper therefore discusses our atom probe tomography results that were performed to elucidate the exact structure of the GP zones.

The miscibility gap for GP zones was first re-assessed taking into account the slow kinetics of the GP zones to reach their equilibrium structure. Indeed, the temporal evolution of GP zones at temperatures below 180°C reveals two regimes: a first stage during which GP zone equilibrates while exhibiting complex morphologies and a second stage of coarsening once the GP zones have reached their equilibrium concentration of 65 at.% Ag.

In order to understand the limiting mechanism for the equilibration of the GP zones, the temporal evolution of zones formed at high temperature and therefore containing only 35 at.% Ag was followed during aging at low temperature where their equilibrium concentration is 65 at.% Ag. The measured Ag concentration profiles in GP zones can be explained by inwards diffusion of Ag within the Ag rich zones. These observations show that diffusion of Ag in the GP zones is more than an order of magnitude slower than diffusion of Ag in the Al matrix. This discrepancy accounts for the slow kinetics of equilibration at early times and the formation of complex structures that led to the original controversy about the exact structure of the GP zones. To conclude, our work highlights the important role of solute-vacancy interactions controlling the kinetics pathway in phase decomposition. It also emphasizes a renewed understanding of physical metallurgy through the capability of atomic scale 3D imaging (with atom probe tomography) and its combination with theoretical approaches.

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Three-Dimensional Analysis of Semiconductor Device Structures Using LEAP

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A Local Electrode Atom Probe (LEAP) equipped with a pulsed-laser module has been used to study several types of semiconductor structures. The analyzed structures will include a Si/SiGe multilayer stack with and without boron doping and a patterned and implanted phosphorus structure. Nickel germanosilicide structures may also be discussed. The results from these analyses, including 3D atomic maps and 1-D composition profiles extracted from them, will be presented and be compared to Transmission Electron Microscopy (TEM) and Secondary Ion Mass Spectrometry (SIMS) results.

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Cryo-EM of Biological Nano-Machine and Cell

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Cryo-EM has been advanced to record images of frozen, hydrated biological nano-machines beyond 0.4 nm. The images are generally noisy because of the constraints of low dosage. Image processing is an integral component of the research with which 3-dimensional density map can be computed from hundreds to thousands of images of individual single nano-machines in different orientations. If the structural conformations of each of the nano-machines are uniform, one can combine them coherently to generate a 3-D density map as good as the data quality allows. The current state of the art reconstruction has reached the resolution close to 0.4 nm at which the C α backbone of the protein subunit in the nano-machine can be resolved. However, if the conformations of the nano-machine vary from particle to particle, the resolution of the reconstruction would be limited. Image processing is being developed to sort out images according to their respective conformations and the map resolutions of those data so far are still relatively low (1.5-3 nm).

Cryo-EM is also capable of imaging frozen, hydrated cells. The challenge in studying cell is that no one cell is identical to another cell. Therefore, the single particle averaging methodology cannot be applied to the cell images. Cryo-electron tomography is used to collect the 3-D image data from different tilt views of a single cell and the data is constrained by radiation damage. The tomographic reconstruction followed by averaging of extracted molecular components would produce 3-D map at molecular resolution (2.5-4 nm). This approach allows one to examine the molecular conformation, which may be different from that of the biochemically isolated one. The emerging capability of cryo-EM to image single nano-machines and single cells provides the physical basis of understanding their structure and function relationship at a broad spatial range and within the biological context.

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Low-Dose Aberration Corrected Cryo-Electron Microscopy of Organic/Biological Specimens

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Electron microscopy of biological specimens has contributed a wealth of information for cellular biology, molecular biology and pharmaceutical research. Biological samples usually require hydration, are sensitive to the electron beam, and their lightweight atoms carbon, nitrogen, oxygen and hydrogen provide only weak contrast. This so far has forced biological transmission electron microscopy to operate under low-dose conditions with a highly defocused objective lens to increase phase contrast. Under such conditions, images of frozen hydrated samples show an extremely weak signal to noise ratio.

Electron crystallography of two-dimensional membrane protein crystals allows nevertheless obtaining high-resolution information in the 2 Angstrom range, because the signal can be retrieved by computer image processing from the noisy images. Electron crystallography, however, requires well-contrasted images that contain the high-resolution data.

Spherical aberration (C_s) correction in the Transmission Electron Microscope has enabled sub-angstrom resolution imaging of inorganic materials. To achieve similar resolution for radiation sensitive organic materials requires the microscope to be operated under hybrid conditions: low electron dose at the specimen at liquid nitrogen temperature (optimum for organics) and low defocus values (optimum for inorganics). Initial images from standard inorganic and organic test specimens have indicated that under these conditions C_s -correction can provide a significant improvement in resolution (to less than 0.16 nm) for direct imaging of organic/biological samples.

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Needs for Next-Generation EM Instrumentation in Structural Biology

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Transmission electron microscopy in structural biology puts a strong emphasis on cryo techniques for the determination of native 3-D structure. In the case of tissue and cells, cryo-electron tomography is the technique of choice, while “single-particle” techniques are used to provide near-atomic-resolution maps of macromolecular complexes. Ideally, the two techniques are combined to investigate *in-situ* configurations, and map the macromolecules within cells. It has long been recognized that the extreme radiation sensitivity of native biological specimens presents a serious challenge for obtaining high-resolution results, and efforts over many years have focused on improving contrast without increasing the electron dose. The dose problem is especially severe for cryo-electron tomography, in the effort to obtain 2-3-nm-resolution for the 3-D structure of native, unique, asymmetric specimens.

Zero-loss energy filtering is now considered essential for cryo-tomography of all but the thinnest specimens, doubling the contrast for typical specimens. Further gains will be realized by improved cameras using new detectors now under development. We are focusing on use of an objective lens back-focal-plane phase plate, which gives an (additional) improvement in contrast on the same order as zero-loss energy filtering, and also simplifies image interpretation, by facilitating in-focus phase-contrast imaging that avoids oscillations in the contrast transfer function. In the future, aberration correction (both C_s and C_c) promises to provide important gains, especially in the case of thin specimens imaged at moderate acceleration voltage.

The ideal next-generation cryo-TEM for structural biology would operate over a wide range of accelerating voltage, and employ a modular approach to allow upgrades as the technology improves.

At the same time, improvements in specimen preparation and handling are needed. In cryo-tomography, better methods are needed to produce undistorted specimens of vitreously frozen cells and tissue. Our work has shown that cryo focused-ion-beam (FIB) milling is a promising technique. Instrumentation is being developed to select a site in the specimen, prepare a thin specimen at the site, and conveniently transfer the specimen to the TEM for tomography. In single-particle work, automated specimen preparation, integrated with TEM automation for selection of specimen areas containing good particles, and unattended recording of a large number of images, is proving its worth, and will become standard in structural biology EM laboratories.

“Time Resolved” 3-Dimensional Cryo-TEM to Study CaCO₃ Crystallization on a Self-Organized Organic Template

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In Nature, many organisms show very complex forms composed of inorganic materials, of which of calcium carbonate is one of the most abundant ones.¹ These materials are formed by crystallization of the inorganic material on template consisting of an organized organic matrix. It has been shown that the nature of the organic template influences polymorph selection, crystallographic orientation, as well as the morphology of the developing inorganic materials crystals. Inspired by these biological systems, the biomimetically controlled crystallization of calcium carbonate is explored for the formation of new biomaterials.

In the present study, we use precisely defined self-assembled models in order to understand in detail the role of the organic templates in the first steps of the mineralization. The templated mineralization of CaCO₃ is studied using bis-urea surfactants that self-organize by hydrogen bonding giving rise to ordered closed packed sheets. Importantly, studies on the mechanisms of nucleation frequently rely on the characterization of mature crystals or on the study of early crystals after transfer to TEM grids etc. Although it is generally accepted that important interactions and changes take place in the early stages of the nucleation process only few reports exist in which *in situ* techniques are employed to study biomimetic mineral formation.^{2,3} Especially important in this respect is the role of amorphous calcium carbonate.⁴

Here we present a new method for the time resolved monitoring of the nucleation of calcium carbonate under self-organized surfactant monolayers by cryo-TEM combined with electron diffraction. With this technique we are able to study the conversion of amorphous calcium carbonate into oriented calcite. In addition, cryo-electron tomography allows a 3D view of the developing CaCO₃ particles and their interaction with the template. First results indicate that in the very early stages small amorphous particles are formed in solution before oriented nucleation occurs on the template.

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Fifty Years Old and Still Going Strong

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Although the first observations of dislocations by transmission electron microscopy were made just over fifty years ago, the technique is if anything more important now than it was then. The advent of scanning transmission microscopy opened the world of chemical information to investigation, and the development of aberration-corrected microscopes has enabled sub-atomic resolution. Electron microscopy is still far from its fundamental limits, and will continue to play a central role in interdisciplinary studies of nanostructures. Modern students need to be educated in a wide range of physical science if they are to tackle the exciting problems that lie ahead.

Deformations in Carbon Nanotubes and Metal Nanoparticles: Results from Modeling Coherent Nanoarea Electron Diffraction Patterns

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High quality coherent diffraction patterns can be recorded from individual nanostructures using an electron probe of few tens of nanometers in diameters. So far, electron is the only probe capable of doing this. The advantage of recording diffraction patterns is that diffraction intensity can be quantified, but interpretation of diffraction patterns often requires modeling. What we can learn about materials structure from modeling diffraction patterns often goes beyond what we can see in electron images. Here, using two examples, we illustrate an approach of nanostructure modeling and comparison with experimental diffraction patterns. In the first case, we study the deformation of carbon nanotubes in a two tube bundle. We modeled nanotube deformation using molecular dynamics simulation. By simulating the diffraction patterns of deformed tubes, we show that certain layer lines of the helical diffraction pattern of a carbon nanotube are sensitive to tube deformation. Using this information, we compared with the experimental diffraction pattern and measured the amount of deformation in a real tube. In the second case, we compared the diffraction pattern from a single Au nanoparticle with models obtained from molecular dynamics simulations and chemistry. We show that the nanoparticle diffraction pattern is characterized by asymmetry which comes from surface contraction of the nanoparticle. The principles of analysis used here are general and applicable to other nanostructures. Unique structural information can be obtained from coherent electron diffraction patterns where we can start to learn about the peculiarities of nanostructures.

Recent Development of Soft-X-ray Emission Spectroscopy Instruments for a Conventional Analytical Transmission Electron Microscope

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Characterization with nm-scale spatial resolution is important for developments of new functional materials. A development of a soft-X-ray emission spectroscopy (XES) instrument, referred as the original spectrometer, for a transmission electron microscope (TEM) presented us that a density of states (DOS) of the valence band can be obtained from a specified small specimen area [1]. It implies that the DOS of the valence band by XES and the conduction band by EELS can be obtainable based on a transmission electron microscopy [2]. Furthermore, the spectrometer dose not disturb the spatial resolution of a TEM, because it does not have a moving mechanism as in a case of WDS spectrometers of EPMA.

A project to renew the spectrometer to attach to a conventional analytical TEM has been conducted. Two types of spectrometers, a high-dispersion type and a commercial type, have developed for a conventional TEM. Those spectrometers are composed of laminar-type varied-line-spacing (VLS) gratings, a CCD detector and X-ray collection mirrors. The measurable energy range is 60 – 1200 eV. For example, the best energy resolution has confirmed to be 0.2 eV for Fermi edge of an Al L-emission spectrum at about 70 eV [3].

For applications to materials science, it is important to extend the measurable energy range to higher energy region. As a first step, a multilayer-coated (MLC) VLS grating optics has designed and manufactured for the high-dispersion type spectrometer to extend a measurable energy range up to 2 keV. This spectrometer can set four VLS gratings and can measure an energy range from 60 to 2100 eV. The material pair of the multilayer is Mo and C. The period length and total number of periods are 5 nm and 30, respectively. A mechanical control unit of the tilt angle of the grating for incident X-ray has introduced to realize optimum diffraction efficiency conditions for different X-ray energies. Other three VLS gratings are used for fixed angles of X-ray incidence. The test measurements of Si K-emission shoed that a FWHM value of the K α peak (1740 eV) of the new spectrometer is reduced by a factor of 4.4 compared to that of conventional one. Si K β -emission peak (1836 eV) is also clearly observed, which is only a tiny hump on the tail of M α -peak for a conventional EDS spectrum. Pt M-emission peaks, M α (2050 eV) and M β (2127 eV), have also measured using the new spectrometer. A FWHM value of the M α peak was 13 eV.

This project is conducted under a name of “Development of an EELS/XES electron microscope for electronic structure analyses”, which is one of the leading projects of Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Electron Energy-Loss Spectroscopy of Surface Excitations near Interband Transitions in Nanomaterials

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There are two generally known collective excitations localized on the surface of a material, namely, surface plasmons in the metallic spectral regime and the guided surface modes in the transparent spectral regime below the band gaps. In this talk, I'll discuss a rare kind of surface excitations which occur in a spectral regime near strong interband transitions where the real part of the dielectric function is positive and the imaginary part exhibits a maximum due to intense optical absorption. This type of surface excitation bears strong resemblance to the so-called surface exciton-polaritons observed largely in semiconductors at low temperatures. Using electron energy-loss spectroscopy (EELS) with a 2-Å electron probe in a loof (near-field) geometry and energy-filtered imaging in real space, we firmly establish the existence of this unconventional surface excitation on the surfaces of GaN, AlN, and ZnO nanorods. Moreover, the surface exciton-polariton-like excitations are also observed in individual Au nanoparticles in the far-UV, non-metallic spectral regime (≥ 10 eV) where the real part of the dielectric function is positive. In this spectral regime, the optical and electronic properties of Au are dominated by the interband transitions from deep $6sp$ - and $5d$ -bands.

Mapping Electron Excitations in the Visible-UV Range Using Sub-nm Resolved STEM-EELS Spectrum Imaging

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For decades, the electron energy loss spectroscopy (EELS) in a transmission electron microscope has been used to explore electronic and electromagnetic excitations of solids. In particular, the low-loss energy domain (from few eV to 50 eV) has been exploited for studying the dielectric properties of materials. However, so far, only excitations in the UV range and above were investigated due to severe limitations in the detection of lower energy spectral features hidden by the strong contribution of the transmitted beam to the measured spectrum. The EELS spectrum-imaging mode in a scanning transmission electron microscope allows to record the variation of the EELS signal at a sub-nanometer scale. Therefore, by combining the spectrum-imaging approach with recently developed *a posteriori* deconvolution techniques it is now possible to probe with unprecedented spatial resolution spectral features that were so far only measurable with optical techniques. With the support of well adapted models to simulate the optical response of nano-objects and the associated local low-loss EEL spectra, these new possibilities open the route to the exploration of a large variety of new problematics in nanophysics. Some examples will be reviewed:

- The delocalisation effects of interface plasmons in dielectric multilayers and the consequences on the estimation of the optical gap of such heterostructures [1]
- The optical response of individual silver nanoparticles [2]. More specifically, from the mapping of the different plasmon excitations in the visible range, the interplay between local effects (local electromagnetic field enhancement) and long range effects (symmetry of the excitation modes) will be discussed.
- The optical response of dimers of silver nanoparticles.
- The optical response of new types of gold nanoparticles, namely nanodecahedra and nanostars. The analogies and differences between EELS and optical measurements will be also stressed, emphasizing that the quantity measured in both EELS and optical near field microscopy, namely the Local Electromagnetic Density of States, is the same [3].

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Electron Energy-Loss and X-ray Spectrum Imaging for Materials Characterization in Aberration-Corrected Scanning Transmission Electron Microscopes

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Aberration-corrected scanning transmission electron microscopes (STEMs) have attracted considerable attention due to the superior performance in both high-resolution imaging and analysis. Using such aberration-corrected STEMs, image resolution has already reached sub-Ångstrom levels in high-angle annular dark-field (HAADF) imaging, which is one of the primary applications of the aberration-corrected STEMs. Since the image resolution in HAADF-STEM imaging is directly related to an incident probe size, the aberration correction provides significant improvement in resolution. Furthermore, a signal-to-noise ratio in imaging can also be improved because the peak intensity of the incident probe is significantly enhanced by the aberration correction. With these improvements, it is now routinely possible to detect small atomic-number difference (less than 3) in atomic-resolution HAADF-STEM imaging.

In addition, aberration-corrected STEMs are also useful for electron energy-loss spectrometry (EELS) and X-ray energy dispersive spectrometry (XEDS) analysis since more beam current can be added into the probe while still maintaining a fine probe. For example, resolutions of 1.4 and 2 Å are still achievable with the beam currents of 100 and 500 pA, respectively, in the aberration-corrected mode, which are at least 10 times higher current than that in the conventional instruments. Especially for EELS analysis, such higher beam currents are sufficient enough to generate core-loss signals for reasonable analysis within a short acquisition time. So, it is possible to acquire EEL spectrum images from individual atomic columns. In combination of spectrum imaging with multivariate statistical analysis (MSA), it has been confirmed that EELS intensities vary related to atomic positions. For XEDS, spatial resolution below 1 nm is now achievable due to the refined probe by the aberration correction. Besides the spatial resolution, the detectability limit in terms of minimum detectable atoms is improved because the X-ray excited region defined as the analytical volume is reduced with the refined probe. In combination with MSA, analytical sensitivity and spatial resolution in the aberration-corrected STEMs are approaching those of atom probe tomography. The superior imaging and analytical capabilities in the aberration-corrected STEMs will be essential for atomic-scale characterization of nanostructured materials and will be routinely available in the new TEAM microscopes as well.

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Applications, Limits and Prospects of Valence Electron Energy-Loss Spectroscopy in Transmission Electron Microscopy

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Much of what is known about the electronic structure of nanomaterials is either based on theory and models of individual particles or derived from experimental methods that due to a lack of spatial resolution measure integral electronic properties of ensembles of nanoparticles. What generally cannot be ruled out is that the response of an ensemble of particles differs from the response of an individual particle. Valence electron energy-loss spectroscopy (VEELS) in a (scanning) transmission electron microscope provides the spatial resolution to locally analyze heterogeneous nanomaterials and to measure band-structure information of individual nanoparticles¹. Furthermore, combining the benefits of an electron monochromator with an illumination aberration corrector, the experimental conditions can be tailored according to the requirements of the material under investigation; size and current of the electron probe as well as energy resolution and primary electron energy are adjustable over a broad parameter range. This enhanced flexibility simplifies the application of VEELS on the nanoscale.

Although numerous examples in the literature demonstrate that VEELS is a reliable technique to identify band-structure information of (nano-)materials, the information content of VEEL spectra is controversial. Surface, finite sample size and retardation contribution can alter the dielectric losses measured by VEELS². Dielectric theory^{3,4} however provides a mean to critically check experimental data and, provided that dielectric data are available, to forecast spurious VEELS contributions. Here we present a study of the low-loss electron scattering of three different samples; bulk Si, InN grown on sapphire and CdSe quantum dots on a Si₃N₄ support film. Comparing experimental results with theory, it is shown that retardation contributions can significantly alter the dielectric losses in VEEL spectra and thus hamper a subsequent Kramers-Kronig analysis. However, the severity of their impact and the type of retardation contribution depend on the material. For Si, an absorption peak due to the excitation of a guided light mode interferes with the dielectric losses, whereas in the cases of InN and CdSe/Si₃N₄ the impact of a smooth retardation contribution does not impair the determination of band transition energies.

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Preparation of High-Quality TEM Specimens of Some Metals and Alloys via a Novel Integration of Chemical-Mechanical Polishing (CMP) with Wedge Polishing

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The quality of TEM analysis depends heavily upon the quality of the specimen. Much effort has been made and various schemes have been proposed to prepare better TEM specimens.

A commonly-used way of TEM specimen preparation for metals and alloys is the electrolytic polishing or electrochemical polishing after mechanical thinning steps, such as sectioning and the subsequent grinding. Hazardous electrolytes like nitric acids and sulfuric acids are generally employed.

If higher specimen throughput is required, the Focused Ion Beam (FIB) machining systems is usually considered. However a FIB machine may cost almost the same magnitude of the total price of a TEM. For most materials research laboratories, this is too plenty of money to spend for just a TEM specimen preparation tool [1].

In the field of failure analysis of modern semiconductor industries, wedge polishing methods have been proved to be successful in preparing TEM specimens of Si-based devices [2]. In such schemes, specimens are first polished mechanically into wedge shapes to guarantee the existence of thin area. After subsequent chemical-mechanical polishing (CMP) processes, damage-free specimens with large electron-transparent areas can be obtained. For some semiconductor materials, TEM-ready specimens can be obtained even without the process of ion milling [3]. But for metallic materials, especially for aluminium and its alloys, there have never been any examples or even attempts to prepare TEM specimens by the combination of wedge polishing with chemical-mechanical polishing.

Based on the remarkable surface-finishing capability of the CMP process, a new scheme is proposed here to prepare high-quality TEM specimens of some metals and alloys by integrating the wedge polishing together with chemical-mechanical polishing. Preliminary study shows that this novel specimen preparation scheme does yield excellent TEM results for pure aluminium and its alloys without the use of dangerous electrolytes. And the problems associated with electropolishing such as the cooling during operation and the disposals of the waste chemicals afterwards, were avoided.

Further studies concerning about the modification of the wedge polishing procedures, the effect of different CMP slurries etc., will be discussed in details.

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New Method for Very Large 90° Slope Cuts

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In recent years ion beam slope cutting has been developed to one of the most applicable method for cross-sectional SEM sample preparation. It can be used to reveal interfaces or internal structures of the sample. Slope cutting is mostly the only way to prepare porous materials, brittle materials or material combinations having wide differences in hardness such as semiconductor materials.

The initial version of this method developed by Hauffe in 1977 [1] can be used for slope cuts in the range from a few micrometers to maximum 50 micrometers length. The classic ion beam slope cutting method is using one ion gun and a sample oscillation to avoid surface structures due to different milling rates. The disadvantages are the milling length limitation, the long preparation time, re-depositions and shadowing effects caused by different milling rates of the structural components.

Consequently, the classic method does not meet today's requirements regarding cut length and preparation time. Especially the semiconductor industry is interested in very long cuts of integrated circuits and packages up to 1 mm in high quality.

To overcome these disadvantages we have developed a new method. The basic idea is the application of more than one ion beam [2]. We have used 3 ion beams hitting the sample from three different directions. Beginning from the perpendicular direction of incidence the angle between each ion beam is 50°, consequently the full milling sector is 100°. The multiple beam method can be used instead of sample oscillation to avoid preferential structures on the slope. On the other hand the milling rate is more than three times higher compared to the classic method. This offers the opportunity to prepare very long cuts in a short preparation time. We are able to prepare extended slope cuts in all dimensions. A cut of 1mm in length and more than 4 mm in width is now possible in less than 10 hours. Furthermore, it is possible to cut very deep into the material. Prepared bump structures proof the high preparation quality. The solder bump and its intermetallic compound (IMC) are very flat and clean. Particularly the structural details of the IMC, such as grain structure and voids in the interface are clearly visible. Surface structures due to different milling rates could be avoided.

The new slope cutting method allows a step in a new area of sample preparation. Furthermore, the method is time and cost saving.

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In Situ TEM Nanoindentation of a 50nm Particle: Observed Deformation Mechanisms and Theoretical Analysis

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Nanoindentation of nanostructured materials is a very rapidly growing area of investigation. Many experiments have tested nanostructured materials of various sizes, shapes, and compositions to determine the fundamental effects of length scale constraints on the mechanical behavior of materials. To this end, an *in-situ* deformation experiment was performed on a single crystal nanoparticle with a diameter of approximately 50nm. Evidence dislocation nucleation and dislocation motion was observed during in-situ TEM nanoindentation, but upon unloading dislocations were no longer visible. The TEM observations provide insight into the plastic deformation mechanisms available to nanoparticles and are of great interest in the interpretation of other recent nanoindentation experiments. Additionally, the experiment provides insight into how nanomaterials behave under deformation.. Because observed dislocations intersected the particle's surface, both the dislocation loop and image force only assumptions made by previous models explaining dislocation behavior are inadequate for addressing the situation observed in the nano-indentation experiment. Additionally, several dislocation dynamics models developed for nano-pillar indentation are inappropriate because dislocations are not seen to nucleate from Frank-Read sources. Therefore, a new analytical model for explaining dislocation instability is introduced. The application of this model to the deformation behavior of nanomaterials is also considered.

In-Situ TEM Study of the Interaction of Dislocations with Stacking-Fault Tetrahedra at Elevated Temperatures

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The mechanical properties of materials are altered by exposure to irradiation. For example, the yield and tensile strength increase is accompanied by a marked loss of ductility – the irradiation embrittlement of the material. The microstructure in the deformed material is characterized by distinct defect-free regions (dislocation channels). To construct physically-based models that can predict the macroscopic mechanical response of irradiated alloys requires an understanding of the controlling fundamental deformation mechanisms and processes, including understanding the processes by which dislocations interact with and annihilate the defects. Such models are needed to accelerate the design, testing and verification of new alloys with properties tailored for next generation energy systems and to enable interpretation of accelerated test data to lifetime prediction models. In this investigation, we report on how test temperature impacts the interaction between glissile dislocations and stacking-fault tetrahedra. Large stacking-fault tetrahedra (average size of 51.18 ± 11.43) were produced in gold by annealing and rapid quenching. The interactions were observed at temperature in real time by deforming the sample at nominal temperatures between 573 K and 773 K in a single-tilt heating straining holder. The experiment at high temperature show the interaction with dislocations and stacking-fault tetrahedra and illustrated different types of interactions that include: Shearing of the tetrahedron followed by its complete restoration, absorption of the stacking fault tetrahedron on the dislocation and its subsequent annihilation, and conversion of a tetrahedron to another defect type.

The nature of the interaction depends on the dislocation character, edge or screw; the tetrahedron type, fully formed or truncated; and the point of impact of the dislocation on the face of the tetrahedron. To gain insight to the atomistic processes controlling these interactions, the experimental observations have been compared with results obtained from molecular dynamics computer simulations. Despite the obvious difference in strain rate and stress, the two approaches show striking similarities that aid the interpretation of the interactions. In general, no significant effect of the test temperature is observed. The implications of these observations in the construction of a physically- based predictive model will be discussed.

Length Scale Effect on Failure of Thin Free-Standing Aluminum Films

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Failure analysis of thin free-standing aluminum films in a transmission electron microscope (TEM) revealed that the failure was highly dependent on film thickness. Aluminum films of varying length, 50 to 300 μm , and thickness, 125 to 500 nm were investigated. The free-standing beams were directly incorporated into a MEMS based tensile testing device designed to ensure application of uniaxial tension. All samples were examined post-failure in the TEM. It was determined that the failure was nominally independent of gauge length, but was strongly correlated to gauge thickness. Shear fracture with complex dislocation structures exhibited several grains from the fracture surface into the film was observed in the 500 nm thick films. Scanning electron microscopy (SEM) revealed a knife edge fracture confirming extensive local plasticity during failure. In contrast, 125 nm thick films failed intergranularly and perpendicular to the tensile direction with limited evidence for plasticity. A similar behavior occurred in the 150 nm thick films signs of limited plasticity in grains near the fracture surface. The observed dependence of fracture mode and mechanism on film thickness in fracture suggests a length scale effect. It is postulated that as film thickness is decreased the surface roughness and flaw size to relative gauge thickness is increased resulting in the transition in failure mechanism and resulting fracture surface. These findings have implications of results published in the literature and these will be discussed.

Development of an Ultra-Fast TEM Heating Stage

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A new transmission electron microscope (TEM) heating stage has been developed to investigate nanoscale phenomena. This stage, produced by a combination of traditional machining and microfabrication, offers significant advantages over conventional high temperature stages. The TEM holder operates at temperatures as high as 1200 °C and can reach this in approximately 1/1000th s. The stage also offers rapid cooling rates, rapid image stabilization, minimal sample drift at high temperature, and the ability to conduct multiple independent experiments on one device. A disadvantage is that the microfabricated heating devices are intended for single use and the current design is single tilt.

In order to demonstrate the capabilities of the stage, results from two preliminary experiments will be presented. First, single walled carbon nanotubes (SWCNT) and SWCNT bundles were heated to approximately 1200 °C and then repeatedly cycled to room temperature. While the majority of the structures showed no response to the drastic temperature changes, a limited number of SWCNT fail. Secondly, colloidal gold nanoparticles, approximately 12 nm in diameter, were heated and observed *in situ*. Particles were observed to first merge with vicinal gold particles before undergoing Oswald ripening. These preliminary investigations into the thermal stability of nanomaterials under extreme thermal conditions exemplify the usefulness of this new stage in nanosciences, and highlight the breadth of its capabilities.

In-Situ Investigation of Growth Mechanisms of Single-Walled Carbon Nanotubes Using Environmental Transmission Electron Microscopy (E-TEM)

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In order for single-walled carbon nanotubes (SWCNTs) to be incorporated as building blocks in future electronics, it is necessary to control their structure, as this is known to strongly affect their electronic properties. The primary motivation of our work is to investigate the exact growth mechanisms during catalytic chemical vapor deposition (CCVD) of SWCNTs.

Recently, several in-situ experiments using specially designed transmission electron microscopes (TEMs) have revealed significant features of CNT growth, which are not observed in normal ex-situ images. However, more systematic in-situ experiments with higher spatial resolution are still needed to clarify several controversial observations, and thus fully understand the exact growth mechanism of SWCNTs created by CCVD.

For successful in-situ TEM experiments with high spatial resolution images of the catalyst and nanotube structure, two requirements should be satisfied. First, movement of catalysts during SWCNT growth should be minimized to allow more careful characterization of their evolving structure. Second, the concentration of catalysts must be well controlled to allow individual tube growths to be studied from start to finish. The spin-on-catalyst (SOC) method, which has been demonstrated in prior research, is well matched to these requirements. In these experiments, SWCNTs were successfully produced using a high temperature reduction of commercially available $\text{Fe}(\text{NO}_3)_3$ particles in an amorphous SiO_x film on Si substrate. Furthermore, by simply using other transition metal nitrates, we can produce various SOC films with different types of catalysts such as nickel, cobalt, molybdenum, and so on.

We will present details of the sample preparation method based on the SOC approach on different substrates such as nickel, silicon, and silicon nitride coated silicon, which should provide thermal stability at growth temperature for in-situ high resolution imaging. Additionally, we will show that these same films are suitable for SWCNT growth by CCVD. By utilizing electron diffraction and high resolution images combined with electron energy loss spectroscopy (EELS), we will present the detailed characterization of the catalysts, as well as aspects of their coarsening behavior at both temperature and pressure. Also, we anticipate presenting preliminary results from the growth of SWCNTs in-situ to environmental-cell TEM(E-TEM).

Dislocation – Boundary Interactions in Low Stacking-Fault Energy FCC Alloys Observed Using the *In Situ* TEM Deformation Technique

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Development of plasticity models to predict the mechanical response of a material during deformation requires detailed understanding of the interaction of dislocations with grain boundaries. Static observations of materials deformed during quasi-static and high strain rate deformation have shown dislocations are emitted from grain boundary sources in response to these interactions; however, the observations fail to adequately capture the details of the dislocation source mechanism within the boundary. The focus of this work is to reveal the processes controlling dislocation emission from grain boundaries through direct observation. Room temperature *in situ* TEM deformation experiments in Cu-4wt% Al and a nitrogen-strengthened austenitic steel show the, sometimes simultaneous, emission of multiple dislocations with different Burgers vectors from the same area of a grain boundary. The emission is attributed to high levels of localized strain present within the boundary. Propagation rates for the different types of dislocations ejected from different types of grain boundaries are observed to vary possibly due to local interactions of dislocation stress fields. These observations provide insight to the mechanisms controlling the transfer of slip across grain and twin boundaries. A second question that will be addressed concerns the propagation of twinning dislocations through a field of perfect dislocations to establish twins that extend across a grain. Here we identify a new mechanism to account for this feature.

Growth Behaviour of Free-Standing Tungsten-Nanowhiskers on SiO₂ Substrates with EBID in a TEM

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Free-standing tungsten-nanowhiskers about 3 nm in thickness were fabricated on SiO₂ substrates with electron-beam induced deposition (EBID) in a TEM operated at 400 kV at room temperature. Tungsten hexacarbonyl (W(CO)₆) powder was used as a precursor. The current density of the electron beam for the EBID was about $8.3 \times 10^3 \text{ A m}^{-2}$ ($5.2 \times 10^{22} \text{ e m}^{-2} \text{ s}^{-1}$). The growth process of the nanowhisker was observed in-situ, and the nanowhisker was characterized with JEM-ARM1000 TEM operated at 400 or 1000 kV. Nucleus-deposits smaller than 1 nm formed on the surface of the substrate, grew to 2~3 nm and then grew out of the surface to form nanowhiskers under the electron irradiation. The nanowhisker grew long at its tip. The density and growth rate of the nanowhiskers were found to depend on the local condition of the substrate. However, a part of the nanowhiskers grew long to about 20 nm at an approximately constant rate for an irradiation time of 223 s with a total electron dose of $1.16 \times 10^{25} \text{ e m}^{-2}$. The nanowhisker contained nanometer-sized grains of body-centred cubic structural tungsten and an amorphous part. It was found that there exists a critical size about 2-3 nm for a nucleus to grow to a nanowhisker. It is suggested that the nucleation site of the nanowhisker may be controlled by putting appropriate conductive particles in the critical size on the surface of an insulator substrate.

Oxidation Kinetics of Cu Alloys Investigated by *In Situ* UHV-TEM

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The fundamental understanding of oxidation mechanisms has significant impact on many fields including corrosion, heterogeneous catalysis, fuel cells, sensors and oxide thin film processing. Most engineering materials are alloy. For alloy oxidation, most traditional methods focus on the analysis of post-oxidation structures or uniform oxide film growth which cannot provide real time information about nucleation and initial growth of oxide [1,2]. The addition of secondary elements can have dramatic beneficial or detrimental affects on the formation of a passive oxide layer that protects the underlying material from further corrosion. *In situ* ultra high vacuum transmission electron microscopy (UHV-TEM) offers a unique window into understanding oxidation mechanism by directly visualizing nucleation, growth and morphological evolution of oxides at the nanoscale under reaction environments, in the UHV environment necessary for atomically clean surfaces, which enables us to understand the complex kinetics and energetics of selective oxidation of alloys under controlled surface conditions.

Here we present the results of our studies of the initial stages of oxidation of a model alloy, Cu-Ni, by *in situ* UHV-TEM, as an extension of our past oxidation work on Cu and Cu-Au thin films. We compare the behavior of the oxidation of (001)Cu-Ni with that of (001)Cu in terms of the incubation time for oxide nucleation, nucleation density and growth rate of oxide islands. In the Cu-Ni alloy system, two metals form a continuous series of solid solutions at temperatures above 190 °C where the Ni concentration is below 30 at.%. Both elements in the alloy react with oxygen but with different oxygen affinities, and their oxides are insoluble in each other. Our initial results from the oxidation Cu-24at%Ni alloy at $P(O_2)=5\times 10^{-4}$ Torr and $T=600^\circ\text{C}$ show that both Cu_2O and NiO oxide islands form under these experimental conditions, but, unlike Cu(001) and Cu-Au(001) films, are not epitaxially-oriented with respect to the (001) metal alloy film. The mechanism governing these nucleation and growth behaviors of oxide islands in the alloy oxidation will be compared to the oxygen surface diffusion model developed for pure Cu [4] and classical oxidation theories, such as Wagner [1].

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Transmission Electron Microscopy for In-Situ Gas-Solid Reaction and Real-Time Electron Tomography

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We have developed a transmission electron microscope which can image samples at a truly atomic resolution when injecting gas into the sample chamber and/or heating the sample to an elevated temperature. A Hitachi patterned sample holder is required. With another Hitachi sample holder, one can rotate/tilt sample to almost any direction and real-time 3-D electron tomography can be achieved with no missing tilting angle.

In-situ gas environmental transmission electron microscopy (TEM) capability has been developed based on a Hitachi 300 kV high-resolution transmission electron microscope (H-9500) combined with a Hitachi gas injection-heating sample holder. This simple but high performance system allows for dynamic observation and chemical analysis of nanomaterials in-situ, at elevated temperatures with gas environment, and most importantly at atomic resolution. Experimental high-resolution images for in-situ oxidation of Si and SnO₂ crystal growth will be presented. Various nanomaterials were studied to reveal their structural response at high temperatures under gaseous conditions. For example, coalescence of Pt catalysts at 800°C in an air environment was studied. Oxidation-reduction and phase transformation of metallic or semiconducting nanoparticles and nanowires are main focuses in the researches under going. The development of this atomic resolution, in-situ gas-heating TEM system offers an affordable platform for a broad range of user facilities in academic as well as in industry fields to perform gas-solid interaction studies to gain new insights into fundamental behaviors of nanomaterials on an atomic level. The researches will have a great impact on nanoscience and nanotechnology associated with catalysts, fuel cells, environmental safety, gas sensors, geochemistry, and toxicity.

Conventional electron tomography is done by tilting the sample in a transmission electron microscope in a large angle range, e.g. $\pm 70^\circ$, and take images at every incremental tilting angle such as 1° . The 3-D reconstruction can be done in a computer using the recorded series images. The disadvantages of this method include the artifact superimposed on the reconstructed images because of the limited tilting angle range and also the 3D structure can only be obtained after computer reconstruction. Change in thickness after tilting also causes trouble because of the diffraction contrast. We have developed a rotation/tilt sample holder which works with focus ion beam (FIB) system directly. Using FIB, a sample can be prepared into a cylindrical pillar shape with a diameter of less than 100 nm. The pillar can be mounted onto the holder with an assistance of FIB. In Hitachi H-9500 transmission electron microscope, the pillar sample rotates from 0 to 360° while electron beam incidents from a direction normal to the cylindrical axis of the pillar. Images and EDS or EELS spectra can thus be taken in a full 0- 360° range without change in sample thickness. Real-time 3D structure and chemical mapping can be obtained, and artifact can be significantly reduced in 3D reconstruction.

In-Situ Dynamic TEM and EELS Study on the Phase Transition of a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Chalcogenide

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$\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) is being regarded as the most promising candidate for use in nonvolatile phase-change random access memory (PRAM). It exhibits three different phases: amorphous, metastable cubic and stable hexagonal phases. To gain further insight into the structure of GST, it is necessary to understand microstructure behavior of this alloy during heating and cooling which is the basic operation of PRAM device.

Phase transformation and crystal growth behavior of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ were investigated systematically by means of *in situ* heating (from room temperature to 500 °C) of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloy in a high voltage electron microscope with real-time monitoring. Large-scale crystallization occurred to amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ around 200 °C. Large crystal growth developed on heating from 200 °C to 400 °C, and single crystalline grains grew up to 150 nm. Eventually the onset of partial melting of thin $\text{Ge}_2\text{Sb}_2\text{Te}_5$ foil was at 500 °C and liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ was observed for the first time by high-resolution transmission electron microscopy. Hexagonal $\text{Ge}_2\text{Sb}_2\text{Te}_5$ phase remains after a subsequent cooling.

Characteristic 60° dislocations occurred in hexagonal phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin foil cooled from 500°C to room temperature in a high voltage transmission electron microscope. The Burgers vector of dislocation was identified as $1/24 \langle \bar{9}902 \rangle$ which is the edge component of $1/3 \langle \bar{2}110 \rangle$ projected on the $(1\bar{1}20)$ lattice plane. The dislocation resulted from the cooling-induced stress/strain in the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloy.

Investigation of the GST electronic structure was carried out by using the SAIT Titan with monochromator and high energy resolution image filter. The EELS spectra for Sb and Te were accurately assigned.

New Electron Source Concept for Single-Shot Sub-100 fs Electron Diffraction in the 100 keV Range

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We present a method for producing sub-100 fs electron bunches that are suitable for single-shot ultrafast electron diffraction experiments in the 100 keV energy range. On the basis of analytical estimates and state-of-the-art particle tracking simulations [1] we show that it is possible to create 100 keV, 0.1 pC, sub-100 fs electron bunches with a spotsize smaller than 500 micron and a transverse coherence length of several nanometers.

The idea is to make use of a space-charge driven expansion to produce electron bunches that have linear velocity-position-correlations. Such bunches can be created by femtosecond photoemission with transversely shaped laser pulses [2]. The reversibility of such bunches enables 6-dimensional phase-space imaging of the electron bunch. Transverse compression is accomplished by regular solenoid lenses. Longitudinal compression can be accomplished by using radio-frequency (RF) fields to invert the longitudinal velocity-position correlation in such a way that electrons at the rear of the bunch have higher velocities than those at the front. This leads to ballistic compression of the bunch in the subsequent drift space.

The proposed table-top set-up relies on established technology only and is presently being built up in our lab.

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Non-Thermal Collapse of the Silicon Lattice Observed by Femtosecond Electron Diffraction

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In semiconductors, the excitation of a high density of carriers can induce an order-to-disorder phase transition due to an abrupt change in the potential energy landscape of the lattice [1]. This phenomenon is known as “non-thermal melting” since the phase transition occurs before the electronic energy dissipates thermally into the lattice through electron-phonon interactions. We used Femtosecond Electron Diffraction (FED) to resolve the dynamics of non-thermal melting in 50 nm nanofabricated freestanding silicon, excited with 387 nm light at an absorbed fluence range of 5-65 mJ/cm². FED is a pump-probe technique in which pulses of electrons are used in transmission diffraction geometry to resolve photo-induced structural changes [2]. Our latest generation electron gun is capable of delivering electron pulses that are ~200 fs in duration with sufficient electron density to probe non-reversible dynamics. The laser pump pulse, centered at 387 nm, is the second harmonic of a Ti:Sapphire regenerative amplified laser system producing pulses of ~180 fs duration. At this photon energy, absorption occurs predominantly via a single photon process across the direct band gap of silicon. Diffraction images were taken before, during, and after excitation at a series of time delays. At the highest excitation level corresponding to ~12% of the valence electrons, the averaged amplitude of the (111), (220) and (311) Bragg peaks was found to decay in <500 fs. This decay was accompanied by an increase in the intensity of inelastic scattering occurring at a comparable time scale. The increase in inelastic scattering has contributions from both a loss of crystalline order and an increase in the lattice temperature. In contrast, at excitations below damage threshold we extracted a relaxation time constant of ~2 ps [3]. The faster decay at the higher excitation level cannot be explained by the thermal relaxation mechanisms which transfers heat from hot carriers to the lattice on a time scale of a few ps. Instead, these much faster dynamics indicate that the process is electronic in nature. Furthermore, fluence dependence measurements revealed that this electronically driven phase transition occurs at excitation levels above ~6% of the valence electron density, with no sharp threshold but rather a smooth transition between the thermal and non-thermal regimes.

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Femtosecond Relativistic Electron Diffraction at the UCLA Pegasus Laboratory

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The Pegasus laboratory at UCLA has been recently commissioned as an advanced photoinjector facility. Illuminating the cathode with an ultrashort UV laser pulse from a state-of-the-art Ti:Sa laser system, ultrashort electron beams of 3-5 MeV energy and 1-10 pC charge are generated. With an X-band rf-deflector we were able to measure sub 150 fs rms electron bunch length. Longitudinal phase space characterization and beam emittance measurements are also performed to fully characterize the quality of the beam. The use of rf photoinjectors as sources for ultrafast electron diffraction has been recently at the center of various theoretical and experimental studies. The UCLA laboratory is the only operating system in the country which has recently demonstrated electron diffraction using a relativistic beam from an rf photoinjector. Diffraction patterns from various metal targets (titanium and aluminum) have been obtained using the beam out of the Pegasus gun. One of the main laboratory mission in the near future is to fully develop the rf photoinjector based ultrafast electron diffraction technique with particular attention to the optimization of the working point of the photoinjector in a low charge ultrashort pulse regime, and to the development of suitable beam diagnostics.

Transient Cellular Structure is Revealed Using Nanosecond *In Situ* TEM

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Reactive Multilayer Foils (RMLF), also called nanostructured metastable intermolecular composites, are layers of polycrystalline reactant materials that go through exothermic, self-propagating reactions when mixing is driven by an external stimulus. The exothermic reaction front reaches temperatures above 1120 K ^[1] and travels at a velocity of ~10m/s governed by interface diffusion. Since RMLFs produce immense heat over a small surface area, they are used in application as localized heat sources for material bonding or biological neutralization. In addition, the periodic nano-construction makes RMLFs relevant for examination of *in situ* progression of interface-controlled diffusion.

Conventional methods lack the necessary combined spatial and time resolution to directly observe nanolayer mixing, leaving details of the reaction unclear. Using the fast time resolution in the Dynamic TEM (DTEM), the transient states have now been observed *in situ*. The DTEM maintains the high spatial resolution of conventional TEM and adds nanosecond time resolution capabilities ^[2]. The DTEM at LLNL uses a high-speed ultraviolet laser pulse to generate a 30 ns long train of photoemitted electrons for “snap-shot” data collection. Plan-view RMLFs are irreversibly reacted inside the DTEM by an infrared sample drive laser, and then the transient states of the reaction front are observed with time-resolved diffraction and imaging.

Single-shot diffraction has been acquired in front of, in line with, and beyond the reaction front region so as to detect the evolution of phase formation and metastable states. Experimental data showing a full cycle of phase transformation from discrete Al and NiV multilayers to the final intermetallic structure of AlNi will be presented. In RMLFs comprising 15nm Al and 10nm Ni-7wt% V bilayers, the AlNi phase is first detected within 300ns after the reaction front has passed. Furthermore, thermal effects of the exothermic behavior in the material are highlighted by diffraction ring broadening.

By utilizing “snap-shot” imaging, the mixing of RMLFs has been directly observed as the dynamic front passes by the DTEM optic axis, showing details of the non-equilibrium morphology and microstructure for the first time. Lines of mass-thickness contrast, due to cellular grain growth often found when interface diffusion is controlling, appear perpendicular to the reaction front and parallel with its direction of travel. This imaging experiment continues with improved spatial resolution as the DTEM is optimized for greater number of coherent electrons in a single pulse ^[3].

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Coherent Diffractive Imaging in Electron Microscopy

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Coherent Diffractive Imaging (CDI) is commonly used in the synchrotron radiation community to reconstruct images from x-ray diffraction patterns. The technique utilizes iterative algorithms to solve the phase problem with little or no a priori information. While it has been previously demonstrated that CDI works for electron diffraction patterns, the ease of high resolution image formation in TEM has largely overshadowed its usefulness. However, recent developments in the fields of both diffractive imaging and electron microscopy have elucidated several areas in which CDI could provide advantages over conventional imaging methods.

In Dynamic Transmission Electron Microscopy (DTEM) stochastic blurring and global space charge effects are detrimental to the spatial resolution of images formed from single electron pulses. It is proposed that these effects can be mitigated by instead forming a diffraction pattern with the electron pulse and using CDI to reconstruct the image. This would enable the study of material dynamics at nanosecond time scales, with spatial resolutions that are currently not possible in conventional DTEM imaging.

Recently x-ray CDI has been used to generate three dimensional models of strain fields inside of nanocrystals by reconstruction from the diffuse scattering around an individual Bragg spot. While strain field analysis is a well developed field in electron microscopy, phase contrast images do not lend themselves well to tomography. By employing CDI it may be possible to gain unprecedented insight into the three dimensional structure of deformation fields in isolated nanocrystals using widely available electron microscopy techniques.

Development of Time Resolved Reflection High-Energy Electron Diffraction System to Study Ultrafast Phases Transition at Surfaces

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The construction of time resolved reflection high-energy electron diffraction (RHEED) system to study ultrafast phase transitions at surfaces is reported. RHEED is a powerful technique for examining the structure of a substrate surface and the surface crystal since it is sensitive to surface roughness, down to monolayer sensitivity. By combining the RHEED system with the time resolved technique it enables us to study the transient non-equilibrium structures which are crucial to the understanding of phase transitions and dynamics at the surface. The time resolved RHEED consists of an amplified femtosecond laser system, a laser-driven electron gun, a magnetic lens, deflection plates, and an image intensifier with a direct coupling CCD camera capable of single electron detection. A femtosecond laser pulse is split into two beams by a beam splitter. The first laser pulse is used to pump the sample system to an excited state. Then the second laser pulse is illuminated to the photocathode of the electron gun to generate an electron packet by means of photoemission. This electron pulse is accelerated to 30 kV and focused by a magnetic lens. The resulting electron pulse impinges on the surface of the sample in a grazing incidence angle and scatters to form the diffraction pattern. The overall dynamics are recorded as a series of diffraction patterns by a probe electron pulse arriving at a known delay time relative to the pump laser pulse. By analyzing the positions, intensities and widths of the characteristic diffraction spots and rings, the structure of the surface and substrate can be determined at a specific time. Here we present the progress in developing time-resolved RHEED. The diffraction patterns of Au film on H-Si(100) which show significant signal-to-noise ratio with atomistic spatial-temporal resolutions will be demonstrated.

Characterization and Reconstruction of Nanolipoprotein Particles (NLPs) by Cryo-EM and Image Reconstruction

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Nanolipoprotein particles (NLPs) are small 10-20 nm diameter assemblies of apolipoproteins and lipids. At Lawrence Livermore National Laboratory (LLNL), we have constructed multiple variants of these assemblies. NLPs have been generated from a variety of lipoproteins, including apolipoprotein AI, apolipoprotein III, apolipoprotein E4 22K, and MSP1T2 (Nanodisc, Inc.). Lipids used included DMPC (bulk of the bilayer material), DMPE (in various amounts), and DPPC. NLPs were made in either the absence or presence of the detergent cholate. We have collected electron microscopy data as a part of the characterization component of this research. Although purified by size exclusion chromatography (SEC), samples are somewhat heterogeneous when analyzed at the nanoscale by negative stain EM. Images reveal a broad range of shape heterogeneity, suggesting variability in conformational flexibility, in fact, modeling studies point to dynamics of inter-helical loop regions within apolipoproteins as being a possible source for observed variation in NLP size. Initial attempts at three-dimensional reconstructions have proven to be challenging due to this size and shape disparity. We are pursuing a strategy of computational size exclusion to group particles into subpopulations based on average particle diameter. We show here results from our ongoing efforts at statistically and computationally subdividing NLP populations to realize greater homogeneity and then generate 3D reconstructions.

In Situ Laser Fabrication of 1D Nanostructures in the Dynamic TEM

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In order to successfully produce nanoscale materials for applications such as optoelectronic devices and sensors, it is vital to have a controlled method of production of the 1-dimensional (1D) nanostructures that make up their foundation. Limitations of current characterization techniques for the nucleation and growth mechanisms for 1D nanocrystalline materials do not allow for the understanding, and future control, of the evolution of texture, morphology and crystal defects during the process. The vapor-liquid-solid (VLS) process first described by Wagner and Ellis is a widely accepted description of how 1D nanostructures, or nanowires (NWs), are formed. The VLS method involves the formation of liquid metal (catalyst) droplets that act as absorption sites for gas-phase reactants. The supersaturated cluster then grows anisotropically into a NW. This mechanism describes NW growth using chemical vapor deposition (CVD), which has been proven to successfully produce crystalline NWs. Other approaches to NW growth are laser-based methods. Hybrid pulsed-laser ablation and CVD (PLA/CVD) methods and laser assisted NW growth at elevated temperatures require the use of a pulsed laser to ablate a pellet target with a gas flowing throughout a tube furnace. With these methods, the amount of variables involved in the experimental methods yields a myriad of different morphologies. In light of the need for control during VLS growth of NWs, in-situ TEM-based growth methods have become increasingly popular. These experiments were limited, however, by the 30Hz frame rate of video acquisition using conventional in-situ TEM.

Using the Dynamic TEM (DTEM), we treated electron transparent targets using a pulsed laser which may be monitored at nanosecond time scales by pulsed photoemission of electrons. Films of Si/Au, SiO₂/Si and GaN were treated with a frequency tripled (355nm) Nd:YAG laser with a 8 ns pulse rate inside a modified JEOL 2000FX TEM. No additional heat or gas was present in the TEM chamber, and thus, NWs were produced by the control of only one variable: laser intensity. By controlling the laser intensity, we could melt or ablate samples to produce NWs. We present the development of GaN and Si NWs by laser-melting and Si NWs produced by laser ablation. Clusters of NWs produced by ablation of a Si-SiO₂ sample were also produced; in this case, a single laser pulse yielded the NWs. The wires resembled those produced during laser assisted growth experiments by Morales and Lieber, yet NW production did not require gas flow or a temperature increase, unlike their experimental apparatus. In each case, the NWs were produced by monitoring only laser energy for ablation or melting. Thus, the DTEM allows for controlled, in-situ, synthesis and characterization of NWs at nanosecond time scales. A complete understanding of the origin of texture, morphology and extended defects in NWs during nucleation and growth will allow for a more comprehensive model of the mechanisms involved in 1D nanostructure production, and hence have a great impact on the future of the use of NWs in electronic device fabrication.

Three Dimensional Reconstruction of Solid Oxide Fuel Cell Electrodes Using Focused Ion Beam - Scanning Electron Microscopy

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Typical solid oxide fuel cell (SOFC) electrodes consist of contiguous electronically and ionically conducting solid phases in an interconnected porous structure. Quantitatively analyzing this microstructure remains a key challenge in connecting materials processing with electrode performance.

This work will describe the application of dual-beam focused ion beam – scanning electron microscopy for three-dimensional reconstruction of Ni-YSZ cermet anodes and (La,Sr)CoO₃ cathodes. Different methods for segmentation – *i.e.* converting images to 3D data sets – are compared in order to determine the tradeoff between calculation accuracy and analysis time. For Ni-YSZ active layers, triple-phase boundary lengths and tortuosities were determined for different compositions. A typical Ni-YSZ active layer yielding good SOFC performance had a TPB length of 4.28×10^6 m/cm³ and a gas-phase tortuosity of ~2. Quantitative analysis of the anode structure has also determined percentages of interconnected versus isolated phases, allowing for a more accurate representation of the electrochemically active anode regions. Two single-phase mixed-conducting LSC cathodes fired at different temperatures were also reconstructed to determine electrode surface area, electrolyte contact area, and gas and solid phase tortuosities. The above structural data is correlated with electrochemical test results.

Sub-Angstrom Resolution Electron Diffractive Imaging of Nanoclusters

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Diffraction-limited, instead of optics-limited, information transfer in a diffraction pattern offers a potential imaging solution to visualize the complex exit wave function at a sub-Å resolution, provided that the missing phases in the pattern can be uniquely retrieved. The exit wave function is a linear function to the projected atomic potential in the kinematical limit, therefore would be an ideal candidate as an input for 3D tomography of individual nanostructures.

Compared to direct imaging, the Fourier amplitude of electron exit wave function is directly recorded in a diffraction pattern, but without the phase. The exit wave function cannot be reconstructed without the phase. But, the amplitudes recorded in a diffraction pattern are unperturbed unlike the nonlinear imaging process and unlimited by the lens aberrations, defocus and other microscope resolution limiting factors. Sub-Å signals are thus available beyond the information limit of direct imaging. Here we report the realization of such an approach and demonstrate the potential of this new imaging technique by using nanometer-sized CdS quantum dots as examples. The solution of the phase problem is achieved using an iterative phase retrieval algorithm. The diffraction patterns were recorded from individual quantum dots using a nanometer-sized, coherent and parallel, electron beam. Complex exit wave functions of several quantum dots at different orientations are reconstructed from the diffraction intensities. Atoms at sub-angstrom distances are resolved. Significant contrast improvement is obtained compared to high resolution electron micrographs. The issues critical to reconstruction will be discussed; these include the quality of electron diffraction patterns, the robustness of the reconstruction algorithms in the presence of experimental noises, the object support and its effect on reconstruction, last but not least important, dynamic scattering of electrons.

Silicon Carbide Nanostructures Induced by Released Iron Nanocatalysts

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Nanoscale materials are currently being exploited as active components for a wide range of applications, such as composite materials, chemical sensing, biomedicine, optoelectronics and nanoelectronics. Enhancing the flexibility of the shape engineering and integrated nanostructures are important for the design of one-dimensional (1D) nanostructures with specific applications. Recently, many efforts have been made to (i) control of the resultant nanoprodut structures; and (ii) arrange the nanostructures into a building block for special devices. Indeed various structures have been achieved in terms of spheres, tubes, wires, cables, sheets and complex branch structures.

Silicon carbide (SiC), an important group IV-IV semiconductor, possesses unique physical and electronic properties. Its band-gap is almost three times as large as that of silicon, the thermal conductivity is over three times that of silicon, and SiC has the ability to operate at very high temperature of 700 °C. Thus, SiC is a suitable material for the fabrication of electronic devices with reduced cooling requirements and operating at high temperature, high power, and high frequency as well as in harsh environments. SiC-based electronics will offer significant potential as a nanoscale alternative to silicon-based devices for molecular electronics technology. In this presentation, we demonstrate that core-shell structured carbon-encapsulated iron nanoparticles can catalyze various SiC nanostructures including nanocones, multi-segmented nanocones, SiC-metal-SiC and Y, T branch junction structures. The migration of the iron nanocrystal from the graphitic carbon shell and agglomeration are visualized by *in situ* transmission electron microscopy (TEM). The resultant SiC nanostructures are analyzed systematically by different electron microscopy techniques, including Z-contrast, energy dispersive X-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS) techniques, electron diffraction and high-resolution transmission electron microscopy (HRTEM).

Three-Dimensional Structures of Supported Au Nanoparticles

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Very small metal clusters can exhibit patterns of reactivity and catalytic activity that are dramatically distinct, and sometimes completely opposite, than behaviors seen with larger clusters. It therefore remains a significant need in research to fundamentally understand and predict the local structure and stability of catalytic materials. Surprisingly, supported nanoclusters that are used in heterogeneous catalysis are described frequently in qualitative terms (e.g. oblate, or raft-like, hemi-truncated or truncated polyhedral). These types of descriptions miss the essential details of the atomic scale structures, the dynamics they embed, and the energy landscapes that define their transformation. Two state of the art methodologies, quantitative scanning transmission electron microscopy (STEM) and synchrotron X-ray absorption fine-structure (XAFS) methodologies will be utilized and specially designed for determining the three-dimensional (3D) structure and structural habits, both individually and as an ensemble, critical for understanding metallic nanoclusters. X-ray absorption fine-structure technique is one of the premiere tools to study both atomic and electronic structure of small ensembles. By determining coordination numbers, bond lengths and their disorder up to the 5th coordination shell, we can reliably determine the size of the nanoparticles, their surface morphology as well as effects of surface disorder in 1-2 nm-size clusters. Complimentary information on site-specific structure and chemistry can be obtained by high-resolution electron microscopy (HREM) and STEM, which has a unique capability for providing structural and spectral information simultaneously. We have recently advanced this imaging method of STEM by correlating the absolute image intensity to the scattering cross-section. With this improvement, we will directly count the number of atoms in a supported nanocluster avoiding complexities associated with coherent diffraction.

We choose Au, Pt and PtRu₅ nanoclusters as model systems. Small, monodisperse Au₁₃ clusters have been prepared via a ligand exchange reaction of alkanethiols onto phosphine-halide gold clusters and then deposited onto TiO₂ support. To remove the ligands, the Au clusters were annealed in air or, alternatively, exposed to reactive oxygen, e.g. ozone or atomic oxygen, at room temperature. Ozone the smallest bare Au particles (1.2 ± 0.5 nm, 40 ± 49 atoms) than those by heating (2.7 ± 0.6 nm, 324 ± 264 atoms). The Au particles formed after atomic oxygen exposure revealed a broad size distribution (2.1 ± 0.7 nm, 72 ± 98 atoms) with an average size in between those produced by the two prior treatments. Although the atomic oxygen treatment produces a large range of particle sizes, this treatment can produce Au particles as small as 1 nm in diameter. A variety of shapes, including faceted hemispherical, spherical, and oblate Au structures were observed by HREM in the atomic oxygen exposed sample.

Cs-Corrected STEM-EELS Application for Si Nano-Dots in SiO₂

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Si nano-dots embedded silicon oxide is applied to non volatile memory due to charge trap property of Si nano-dot. The control of size, density and distribution of the Si nano-dots is very important to memory efficiency. Si nano-dots, however, could not be well observed by using HREM technique.

Recently, Electron energy loss spectroscopy (EELS) analysis in the plasmon region has given capability to investigate the size, density and distribution of Si nano-dots. Usual EELS spectrum in the core loss region, Si and SiO₂ peaks cannot be separated. EELS spectrum in the plasmon region, however, Si and SiO₂ had different peak position so one can distinguish Si nano-dot from SiO₂ layer. Moreover, Si nano-dots could be clearly observed due to strong intensity in plasmon region.

In present study, the size, density and distribution of Si nano-dots in SiO₂ layer fabricated by plasma enhanced chemical vapor deposition (PECVD) were clearly identified by using Cs-corrected TEM (JEM-2100F). And the effects of aperture size, acquisition time and camera length on image resolution will be also discussed.

Analysis of InAsN Quantum Dots by Transmission Electron Microscopy and Photoluminescence

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InAsN quantum dots are a novel material for optical fiber communication applications. It has a smaller lattice mismatch between the quantum dots and host material. This characteristic helps reduce strain and defects induced in fabrication. However, the nitrogen element added into InAs quantum dots often induces defects.

Previously, transmission electron microscopy has never been used to give a detailed analysis of InAsN quantum dots. By using scanning transmission electron microscopy, it can be seen that the InAsN quantum dots have pyramidal shapes. This might be caused by nitrogen incorporated into InAs quantum dots from taking Energy Dispersive X-Ray Spectrometer (EDS) measurements. It was found that indium introduced into wetting layer as well. The quantum dots sized between 10-21nm in diameter and 10nm in height. Although nitrogen could be difficult to incorporate into InAs quantum dots, InAsN quantum dots, however, seems to find to form on curved-surface sites(or called migration lengths) between {001} facets. The emission peak in InAsN quantum dots was longer than InAs quantum dots, ranging from 1250-1350nm, with a plasma power of 130mW. The red-shift phenomenon happened because of excess nitrogen. The resulting emission peak broadened and implies that nitrogen content also affect InAsN quantum dots. The composition distribution and the shape characteristic of InAsN quantum dots were obtained by transmission electron microscopy (TEM), JEOL-2010F and photoluminescence (PL). The phenomenon was obtained along the orientation <100> around InAsN quantum dots.

Cluster Evolution during Reduction of Pt/Alumina Catalysts

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The arrangement of heavy metal atoms in “as-prepared” catalysts on common, high surface area oxide supports is not well understood, notwithstanding decades of study on the preparation and properties of such catalysts. Aging or calcining treatments cause atomic-scale dispersions of heavy metals to agglomerate into discrete crystalline particles of size >2 nm that can be imaged using conventional high-resolution bright-field imaging techniques. High-angle annular dark-field (HAADF), imaging in an aberration-corrected scanning transmission electron microscope (STEM) is the best technique for direct imaging of heavy metal single atoms and multi-atom “rafts” which are pre-cursors of discrete nanoparticles.

The present study illustrates the advanced capability of imaging in an aberration-corrected STEM to characterize catalyst particles, via the example of Pt dispersed on γ -Al₂O₃. Catalysts were prepared by impregnating the support material with 0.35 wt.% Pt and oxidizing the material at 525°C. The resulting oxidized catalyst was imaged in ORNL’s JEOL 2200FS FEG STEM/TEM, which is outfitted with a hexapole aberration-corrector (CEOS GmbH, Heidelberg, Germany) on the probe-forming optics. *Ex situ* exposure of the catalyst to 4%H₂ in Ar for 15 minutes at 300°C was followed by re-examination in the microscope, followed by a subsequent exposure at 350°C for 15 minutes. The goal of the investigation was to determine the evolution of the Pt dispersion from the non-active oxidized condition to the activated, reduced condition.

For the oxidized Pt on γ -Al₂O₃ catalyst, individual Pt atoms were observed randomly decorating the catalyst support. Detailed examination revealed that these were mainly individual Pt atoms. The atoms moved small distances during observation, but were not, in general, highly mobile on the surface unlike amorphous SiO₂. Following the reduction treatment at 300°C, the number of small clusters had increased at the expense of the single Pt atoms. Small rotations of the alumina support following *ex situ* exposure were noticed. Additional reduction at 350°C changed the structure of the Pt metal species only slightly, primarily by increasing the number of atoms in the typical cluster.

50 pm Resolution Aberration-Corrected 300kV Microscope with Cold FEG

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Aberration corrected electron optics have opened sub-Angstrom electron microscope researches. Lately, Nellist *et al.* [1] demonstrated 78 pm resolution image of silicon crystal in scanning transmission electron microscopy (STEM) at 300kV. Technical achievement of 50pm resolution, radius of hydrogen atom, attracts much interest.

We newly developed a spherical aberration (Cs) corrector for STEM (scanning transmission electron microscopy) and TEM (transmission electron microscopy). The corrector is equipped with two dodeca-poles, based on asymmetry optical system, to suppress parasitic aberrations [2]. The TEM/STEM-Cs correctors were fitted in a new microscope column (R005: resolution double nought five) to achieve 50 pm resolution. The new column, mechanically stiff, has a newly designed 300kV cold-field emission gun (CFEG). The R005-STEM with a Schottky-type FEG demonstrated direct imaging of <211> atomic columns of GaN crystal that are separated by 63pm [3].

For R005-STEM, the aberrations up to the 4th order and the 5th order spherical aberration were measured and controlled. Auto-correlation method using Ronchigrams was devised to determine 12 aberration coefficients up to 5th order. The coherently-converged half angle in the Ronchigram was extended to 50 mrad after the present correction, which was 11 mrad before the correction. For R005-TEM, diffractogram Zemlin tableau was used. The TEM Cs-corrector were adjusted 3rd order spherical aberration less than 2 μ m. The total chromatic aberration of the objective lens, including corrector, was suppressed below 1.5 mm. Our new Cs-corrector system, thus, gives a resolution of 50 pm, provided that the energy spread of the CFEG is 0.3eV. An indisputable test for the R005-TEM/STEM with cold FEG has been done to give sound results. We separated 63 pm of Ga-Ga atomic columns in high angle annular dark field STEM image using GaN <211> sample.

The 50 pm resolution is becoming a routine requirement for STEM/TEM studies on nano-science and materials technology including bio-materials. To answer to increasing research applications, in-situ electron microscopy of materials and nano-phenomena in various environments becomes much more important.

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Investigation of Nanoscale Heterogeneous Catalysts Based on the Cluster Size

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Most industrial catalysts are high-surface-area solids such as amorphous or crystalline oxides, onto which an active component (often a metal, metal oxide, or metal sulfide, often including high-Z elements) is dispersed in the form of very small clusters or particles [1,2]. Catalyst performance is sensitive to cluster size. The activities of many catalysts in this class are affected by exposure to air. In this work we attempted to determine whether exposure to air affects the sizes of supported clusters. Having high-Z elements on a light matrix makes high angle annular dark field imaging in scanning transmission electron microscopy (HAADF-STEM) an efficient method to investigate the supported nanoclusters. Imaging with a small probe size allows for accurate cluster size determination; however, this small probe size deteriorates the signal intensity. In this work we describe and quantify the size distribution of individual nanoclusters from STEM images by using a method that produces satisfactory results for the size measurement when compared with theoretical calculations. MgO-supported clusters, decaosmium carbido carbonyl $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ were examined by using a JEOL 2500SE TEM/STEM microscope with a probe size of 0.3 nm and a collection semi-angle of 35-90 mrad. Images were taken at 6,000,000 magnification. We examined samples immediately after synthesis in a vacuum transfer holder to prevent exposure to air, and after 24 hours of exposure to air. As a consequence of the common problem of low signal-to-noise ratio within the intensity profile, it is difficult to measure the cluster size from the raw images. We can smooth the noise in the image by broadening it using a Gaussian blur, in which each pixel is convoluted by a Gaussian distribution function. The Gaussian blurring was applied to raw STEM images with various magnitudes to obtain the intensity profile of each individual cluster. The cluster size was then plotted as a function of the blurring level to yield the intercept value, which represents the size at which the blurring level is zero—or essentially the raw image. The average size is comparable to the average structure of the cluster frame determined by EXAFS spectroscopy [3,4]. A histogram of size distribution characterizing the clusters after exposure to air shows an increase in cluster size. These results demonstrate a significant step towards understanding catalytic function in relation to the size of active catalytic species.

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***In-Situ* Observation of the Equilibrium Shape of a Au-Si Droplet in a Si Crystal**

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The equilibrium shape of Au-Si eutectic liquid inclusions in a crystalline Si matrix has been investigated using *in-situ* transmission electron microscopy. Si substrates were implanted with He ions and then annealed. This resulted in the formation of voids with a size range from a few nanometers to about 50 nm, at a depth of 250 nm. High-purity Au was then dissolved in hydrochloric acid and applied to the silicon surface, and the system was annealed in vacuum at 1000°C for 10 h. Au atoms diffused into the Si during the anneal and precipitated in the voids during the subsequent slow cooling to form face-centered cubic crystals. The resulting precipitates had a truncated octahedral shape, and were bounded by the Si {111}, {110} and {100} planes. When isothermally annealed above the Au-Si eutectic temperature, the precipitates melted, as confirmed by electron diffraction. The Au-Si eutectic liquid inclusions showed larger {111} facets and rounded {100} segments. Analysis of this shape change indicates that the relative interface energy $\gamma\{110\}/\gamma\{111\}$ changed from 1.06 to 1.14, while that of $\gamma\{100\}/\gamma\{111\}$ changed from 1.17 to 1.3. The anisotropy in $\gamma\{100\}/\gamma\{111\}$ increased slightly with temperature, and the {110} facets disappeared at about 600°C. The result shows that Si{111} is the most stable interface co-existing with the Au-Si eutectic liquid, in agreement with the experimental observation that Au-catalyzed Si nanowires grown by the vapor-liquid-solid mechanism most often grow in the Si{111} directions. We will suggest a scheme by which low temperature growth via the vapor-solid-solid mechanism may yield {100} or {110} oriented wires.

Atomic Structure and Ordering in Epitaxial Nanocomposites

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The combination of several microscopy techniques allows for a comprehensive characterization of structure and growth modes for epitaxial nanoparticle composites, including determination of the atomic structure of the embedded nanoparticles and visualization of a novel self-assembled ordering mechanism. We utilize conventional TEM diffraction contrast and high-resolution imaging (HRTEM) as well as high angle annular dark-field imaging in scanning TEM (HAADF-STEM) to study nanocomposites comprised of small semimetallic ErAs particles (1–2 nm) embedded in epitaxial GaAs or InGaAs semiconductor layers grown by molecular beam epitaxy (MBE). Metal/semiconductor composites are of great interest for novel thermoelectric materials, terahertz and plasmonic applications.

(HR)TEM and STEM studies were carried out using a FEI T20 TEM and a field-emission FEI Tecnai F30UT TEM/STEM operated at 300 kV, respectively. HAADF-STEM was used to unambiguously identify the crystal structure of the ErAs particles as rock salt, despite overlap with the matrix through the thickness of the sample used for TEM. Furthermore, we show that the As sublattice is continuous across the interface between the particle and the zinc blende semiconductor. The particle/matrix coherency provided for a “focusing” effect of semiconductor matrix to allow for HAADF-STEM imaging of the particles. Low-magnification cross-sectional HAADF/STEM showed that at large ErAs concentrations (> 3 at%), the particles showed a strong tendency to order on the {114} planes of the semiconductor matrix in both InGaAs and GaAs layers (i.e. independent of any mismatch strain). The ordering was only observed along one of the <110> directions, likely reflecting the strong anisotropy in surface diffusion characteristic of zinc blende (001) surfaces. Bend contours and large off-axis tilts in conventional TEM modes, such as weak-beam imaging, made it difficult to detect particle ordering, which was clearly observed in HAADF-STEM. We will discuss the possible mechanisms for the observed ordering, including surface instabilities driven by Er deposition. We show that if ErAs particles grew on a faceted growth surface, subsequent perturbations of the growth surface were periodically out-of-phase. The high contrast of the particles relative to the matrix in HAADF-STEM readily allowed the measurement of spacing between the layers of ErAs particles as a function of Er concentration and growth parameters.

Conventional bright field and dark field techniques were used to study these nanocomposites over a wide viewing area, in particular the general morphology of particles as a function of Er concentration and growth parameters. We show that particles sizes could only be controlled within a narrow range, due to kinetic constraints imposed by the overgrowing semiconductor. However, particles were found to nucleate with a near constant size, likely needed to stabilize the rock salt structure. To determine accurate particle size and shape distributions, HRTEM imaging was employed.

TEM Analyses of Synthetic Anti-Ferromagnetic (SAF) Nanoparticles Fabricated Using Different Release Layers

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Magnetic nanoparticles (MNPs) are potential candidates for biomedical applications such as cell labeling, bio-magnetic sensing and separation. This involves functionalizing the MNPs with a species that selectively binds to the target analyte, bio-chemically immobilizing the magnetically-labeled analytes on a magnetic sensor chip and then separating them from unwanted entities by rinsing the sensor chip. The amount of analytes present can be determined from the change in sensor output signal when an external magnetic field is applied. Accurate quantification requires that the MNPs be uniform in shape, size, composition and free from clustering. For good signal-to-noise ratio, they should possess high magnetic moments at low applied magnetic fields and no remanence when no magnetic field is applied.

Synthetic Anti-ferromagnetic (SAF) nanoparticles represent a new paradigm of magnetic nanoparticles (MNPs) wherein ferromagnetic components are used to produce monodisperse, low remanence and high moment nanoparticles. Each SAF is composed of two Co₉₀Fe₁₀ layers separated by a non-magnetic ruthenium spacer layer. Tantalum is used as a protective capping layer to passivate and stabilize the nanoparticles when they are suspended in water. Unlike conventional MNPs that are produced via chemical synthesis routes, the SAFs are fabricated on a silicon substrate using nanoimprint lithography (NIL), direct deposition of multilayer films, and harvest in liquid phase using a release process. The utilization of these techniques enables the morphology and composition of each SAF to be accurately controlled.

Structural characterization of SAF nanoparticles fabricated using different release layers was performed by preparation and analyses of Transmission Electron Microscopy (TEM) crosssection specimens from arrays comprising SAF nanoparticles. When copper was used as the release layer, the layered structure of the SAFs was found to be disrupted and wavy multi-layers were observed, due to the formation of copper grains of varying heights from the release layer. When oxygen was introduced into the release layer prior the film deposition process, the topography of the oxidized-copper grains was effectively controlled and consequently, SAF nanoparticles with straight multi-layers were fabricated. This structural improvement also led to a corresponding decrease in the magnetic remanence of the nanoparticles. TEM analyses thus resulted in an important improvement in the structural and magnetic properties of the SAF nanoparticles.

Novel BN Structures and Their Effect on Cubic-BN Nucleation

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Cubic boron nitride (c-BN) nucleation often takes place on turbostratic boron nitride (t-BN) layers. TEM observations showed that these t-BN layers are made up of single sheets of sp^2 bonded BN growing perpendicular to the substrate surface. Studies focused on the nucleation phase of the cubic phase suggest possibility of transient and/or intermediate phases involving highly curved nano-scale structures such as nano-arches and nanotubes, having an influence on the nucleation of sp^3 bonded cubic phase. In this study, effects of deposition parameters, such as ion energy and substrate temperature, on the evolution of these novel nano-scale structures are investigated (see figure 1). Using images from TEM observations, structural models of some of these structures are built. These structures are then used to perform DFT studies comparing the reactivity of such novel structures and understanding their role for the cBN growth.

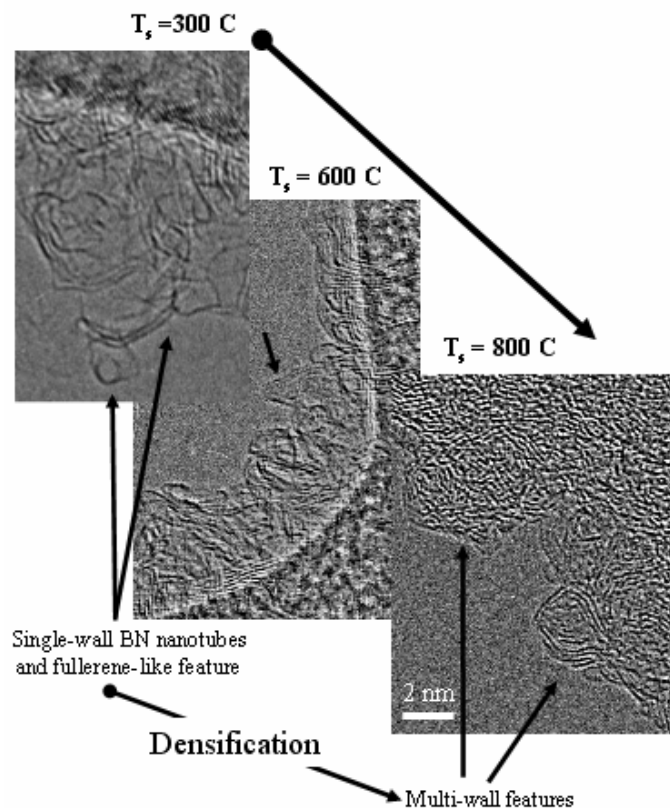


Figure 1. Collage of HREM images from BN films on tungsten substrates displaying the variation in the morphology of the films at increasing substrate temperatures.

Electron Energy Loss Spectroscopy of Carbon Nanotubes and Fullerenes

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Carbon nanomaterials, such as fullerenes and nanotubes, have many potential applications, such as drug carriers [1] and in quantum nanotechnology [2]. In order for these materials to fulfill their potential, it is important to have a good understanding of their properties and how to alter them.

Electron energy loss (EEL) spectroscopy provides a probe of the unoccupied density of states (DOS) of a material. Monochromation of the electron source means that it is possible to get high energy resolution spectra, which, along with simulated spectra, can be used to obtain a better understanding of the electronic structure of a material. Previously this combination of experiment and theory has been used to look at fullerene crystals [3]. In particular, the affect of changes in bond length on the DOS and EEL spectrum has been studied [4].

We are currently extending this investigation to look at the interactions between nanotubes and fullerenes encapsulated inside them. We are using the newly installed monochromated FEI TITAN at Imperial College London to acquire high energy resolution spectra from these peapod systems. This microscope can be operated at 100 kV and the energy resolution is ~ 0.15 eV. We are also looking at several different ways of simulating spectra. We will be presenting our latest results!

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STEM HAADF Analysis of Composite GPB/GPBII Structures in Al-Cu-Mg Alloys

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Aluminum alloys based on the addition of Cu and Mg as the primary alloying elements represent an important class of light-weight structural materials. The metastable phases that allow these alloys to achieve their remarkable strength properties are very poorly understood and are actively being studied. This work attempts to address many of the unresolved issues regarding the metastable phases by application of the STEM HAADF imaging technique, which has proven to be well suited for this type of analysis due to its incoherent imaging nature. The HAADF STEM observations were performed with a probe c_s -uncorrected as well as c_s -corrected FEI Titan 80-300 operated at 300kV.

The observations reveal for the first time the crystallographic nature of these needle-like, nanometer-scale, metastable particles. They are found to predominantly consist of core and shell regions; regions that can be differentiated based on atomic column intensity and the atomic column symmetry. The core region, which tends to have a lath like morphology, is found to have a hexagonal symmetry with lattice parameters $a=0.7$ nm and $c=0.4$ nm. The atomic column positions as projected along the c lattice direction have been fully determined due to employment of a probe-deconvolution technique. This was performed using maximum likelihood method using the Richardson Lucy algorithm as implemented in Matlab®. The shell region, on the other hand, consists of an assembly of sub-nanometer size rod-like units (zones) that can not be described in terms of a periodic crystal structure. The crystallography of this unique structural form, which can be described in terms of point symmetry as m , has been fully determined based on a combination of microscopy observation and ab initio calculations. A strong enthalpy preference of about -0.27 eV per solute atom in the structure as compared to the solid solution approximation is found. Such a significant enthalpy preference provides strong support for the favorability of the structure. Supporting STEM HAADF observations linking this structural form to other stable phases will be also presented.

The relevance of the observations and its relationship to previous X-ray diffraction analyses will be presented. It will also be shown that the observations provide significant insight toward understanding the mechanical properties of this important class of Al alloys.

Characterization and Development of Zirconium Diboride for EDM Electrode Applications

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The present study, reports the fabrication of $\text{ZrB}_2\text{-Cu-Ni}$ cermets with different compositions using hot isostatic pressing (HIP). The effect of relatively small addition of (1-10 wt% Ni) to promote the liquid phase sintering of zirconium diboride has been studied. HIP experiments were carried out at 1400°C under 110 MPa pressure in argon atmosphere. The influence of operating parameters on the microstructure and mechanical properties were also studied. The highest density achieved was over 84% for $\text{ZrB}_2\text{-40 wt\%Cu-5dw\%Ni}$ composite. XRD analysis revealed that there is no formation of reaction products or compounds among ZrB_2 , Cu and Ni. The fracture surface morphology study using SEM reveals the predominantly intergranular fracture. The highest conductivity for the optimized cermet composition is recorded to be 4.05×10^4 siemens/cm. Because of the high electrical conductivity, the newly developed materials are expected to be suitable materials for EDM electrode application.

Effect of Si-Addition on the Precipitates in Al-Mg-Ge Alloys

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It has been well known that the precipitation sequence of Al-Mg-Ge alloys is similar to that of Al-Mg-Si alloys[1]. The analysis of crystal structure, however, has not been reported in detail by the electron diffraction and/or HRTEM observation. In our recent work, precipitates in an Al -1.1 mass% Mg₂Ge (balanced) alloy has been observed by TEM, and the β' -phase and the A-type precipitate were confirmed. The former one is the typical metastable phase in the Al-Mg-Si alloy and the latter one is the major phase in the over-aged Al-Mg-Si alloy including Si in excess. In the present work, precipitates in the balanced Al-Mg-Ge alloy and Al-Mg-Ge alloy with Si have been compared by HRTEM technique to understand role of Si in Al-Mg-Si alloy.

Al -1.1 mass% Mg₂Ge (Al -0.52 at% Mg -0.24 at% Ge, (AMG balanced)) alloy and Al -1.0 mass% Mg₂Ge -0.5 mass%Si (Al -0.95 at% Mg -0.22 at% Ge, (Si-bearing)) alloy were prepared by a conventional casting technique in atmosphere. Ingots obtained were cut and rolled to thin sheets. These sheets were solution heat treated at 873 K for 3.6 ks and quenched into chilled water about 273 K. The aging treatment was performed in a salt bath controlled to 523 K. Thin foils for TEM observation were prepared by a conventional electrolytic polishing method using a solution of 90% ethanol and 10% perchloric acid. HRTEM images, EDS and selected area diffraction (SAED) patterns were obtained by 200 kV (Topcon EM-002B) and 400 kV (JEOL 4010T) TEMs.

Formation and Modulation of an Ultrafine Lamellar Structure in High Nb Containing TiAl Alloys

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Two-phase γ -TiAl based alloys with a fully lamellar structure gain a lot of interest due to their outstanding creep resistance and fracture toughness. It is well known that the spacing of lamellae is the dominant factor determining the mechanical properties, and thus different heat treatments and additives are applied in γ -TiAl based alloys to change the lamellae spacing. In this work, we used conventional and high resolution transmission electron microscopy (HRTEM) to study an ultra fine fully lamellar γ -TiAl / α_2 -Ti₃Al microstructure, which was produced in two Ti-45Al-7.5Nb (in at%) alloys using a two-step heat treatment. The alloys contain either 0.5 at% or no carbon. Firstly, the samples were heat treated for 10min 35K above the α transus temperature (T_α) and subsequently oil quenched to room temperature. Large with Al supersaturated α_2 grains are formed with a small fraction of massively transformed γ_m grains. The specimens were heated with 20K/min up to 790°C or 850°C immediately followed by oil quenching. After that, colonies of ultra fine lamellar structure were observed with an average lamellar spacing down to a few nanometers. It was found that γ respectively α_2 lamellae have already started to form during the first oil quenching from the α -phase region. HRTEM has caught the initial state of lamellae formation in both α_2 and γ_m gains on an atomic scale. The mechanism of lamellar formation in both cases can be explained by Shockley partial dislocations. During the second heating cycle, the nucleated lamellae grow mainly by the movement of ledges. Simultaneously, more atoms at grain boundaries gain enough energy to be mobilized and to nucleate new lamellae. By increasing the second annealing temperature, the thickness of lamellae can be further refined. Besides the temperature, the amount of carbon also has an influence on the lamellae spacing.

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TEM Measurements of Grain Orientation in Nanoscale Cu Interconnects Using ACT Software

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Void formation in Cu interconnects has been a concern for the microelectronics industry due to the fact that they affect the reliability of microelectronic devices. A major reason for this concern is that the mechanisms of void nucleation and growth, and related microstructure are not fully understood. In particular, knowledge of the relationship between void formation and grain orientation in Cu interconnects subjected to thermal stresses is currently lacking.

While electron backscattered diffraction (EBSD) in a scanning electron microscope (SEM) has been instrumental in the past to determine grain orientation in Cu interconnects, downscaling of microelectronic devices has produced Cu interconnects with grain sizes at the nanoscale, which makes the EBSD technique unreliable for grain orientation measurements. A possible alternative method is to use nanobeam diffraction (NBD) in a transmission electron microscope (TEM). However, using NBD coupled with a conventional tilting technique in the TEM is very time consuming.

In this context, to expedite grain orientation analysis in nanoscale Cu interconnects by TEM, we use in this work a software called ACT to measure the crystallographic orientation of multiple grains. The Cu grains and grain boundaries are first identified by tilting over approximately a 20 degree range in the TEM. Once the grain location is determined, a diffraction pattern is acquired on each grain and further indexed by the ACT software. For the 180 nm Cu interconnects analyzed in this work, the results obtained by ACT show that while {111} grains are typically observed, {130}, {100}, and {112} grains have also been noted in other areas of the Cu interconnect. In addition, {011} annealing twins were also observed. The result obtained by the ACT software can then be used as input data in a finite element method to calculate the distribution of local stresses across the microstructure. A total of 34 triple junctions at the Cu/DB interface were observed in three separate experiments. Typically, the voids were observed to form in regions of high local stresses and high stress gradients. In this fashion, a correlation between grain orientation, local stresses and void formation can be obtained.

Ultimative Energy Resolution in an EFTEM with Omega-Type Monochromator

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Electron energy loss spectroscopic (EELS) investigations at high spatial and energy resolution require dispersion-free monochromated illumination. So far, the electrostatic omega-type Monochromator (MC) is the only one which provides dispersion-free illumination, high brightness ($\geq 10^{-8}$ A/cm² sr) [1], and ease of use. The features of corrected in-column Filter [2] are a high transmissivity and dispersion, combined with an excellent isochromaticity. Furthermore, the in-column concept offers the highest flexibility with respect to optimized imaging parameters and selection of image and signal detectors. In this paper we will show that this combination of an electrostatic omega-type monochromator and a corrected in-column filter offers superior analytical capabilities and allow to achieve the ultimative spectroscopic energy resolution.

First of all the MC is advantageous for high resolution work. A reduced energy spread results in smaller damping of the chromatic envelope of the Contrast Transfer Function (CTF). This generates better contrast at high spatial frequencies, and a lower information limit can be achieved which exceeds the 1.0 Å information limit even for an uncorrected TEM. The routinely achievable energy resolution of $\Delta E < 0.2$ eV in EELS mode is in the order of the core-hole lifetime broadening, line splitting caused by core-hole spin-orbit interaction and thus becomes comparable to the energy resolution in X-ray absorption spectroscopy (XAS), but with a dramatic reduction in field of view and complexity of measurement equipment [3]. This opens up new opportunities to extract highly localized structural information from transition metal oxides with negligible interference from instrumental broadening.

The theoretically available energy resolution defined by the slit width and aberrations of the electrostatic Omega-type MC is about 50 meV. Accordingly the stability of the energy filter current and high voltage have to been optimized in order to achieve an energy resolution close to theoretical limit even for long acquisition times. Together with the MPI Stuttgart the stability of both the HT supply and the spectrometer current has been optimized in the SESAM resulting in an energy resolution of 54 meV, which is very close to the theoretical limit. Furthermore the MC provides a steep drop of the tail of the ZLP [5]. Combined with deconvolution techniques [4] this offers dramatic new applications like the measurement of optical properties and phonon spectroscopy.

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**Electrostatic Structure of Ferroelectric Domain
in a Thin Film of BaTiO₃ Fine Ceramics
Observed by 300-kV Electron Holography and Coulomb-Deflection STEM**

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The ferroelectric domain structure in a thin film of BaTiO₃ fine ceramics was observed and analyzed by 300-kV electron holography and Coulomb-deflection scanning transmission electron microscopy (STEM). 300-kV electron holography was used to quantitatively determine the direction and strength of the polarization of a 90° domain in a thin film of BaTiO₃ fine ceramics at medium spatial resolution. To extract the electron phase shift that is intrinsic to the ferroelectricity, we recorded several holograms of the same field of view with the specimen kept above the Curie transition temperature of the material. By subtracting the averaged phase shift from that obtained when the specimen was at ambient temperature, we obtained a phase map due to the electrostatic field associated with ferroelectric polarization. A quantitative analysis of the reconstructed phase map showed good consistency with a computer simulated phase map assuming a model of a 90° domain wall. High spatial resolution images of ferroelectric domain structures were obtained by using 300-kV Coulomb-deflection STEM. The apparatus is an extension of a 200-kV Lorentz-deflection STEM that was successfully applied to observe the magnetic domain structure in a thin film of recording media. A 300-kV electron beam has enabled us observations of thick (>300 nm) specimens. A sub-nanometer electron probe was produced by combining a strongly excited objective lens with a condenser lens having a low aberration coefficient. The local electric field associated with the ferroelectric polarization induces the electrostatic (Coulomb-)deflection of the electron beam, while the local magnetic field associated with magnetization induces the Lorentz-deflection. A two-dimensional map of the amplitude and direction of the in-plane polarization in the specimen at high spatial resolution is thus obtained. With the apparatus, we observed images of 90° and 180° domain walls, a triple junction between the two kinds of walls, and a complex structure at a grain boundary. We also obtained images of novel domain structures and even images of nanodomain structures. Although it is difficult to assess the contribution of the strain effect at the wall, a quantitative reconstruction of the in-plane component of the electric field is possible using a pair of orthogonal deflection images. In this straightforward reconstruction, we found a multiple-layered transition of the in-plane component of the electric field across a 90° domain wall, which is partly consistent with the previously reported quantum mechanical simulation. Interestingly, the applied electric field on the specimen appeared to stabilize the domain structure. At present, we presume that the applied electric field removes the induced electric charge on the surface of the specimen by the focused electron beam, preventing it from accumulating in the field of observation.

Vector Field Electron Tomography: Theoretical Developments

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The main goal of tomography is the reconstruction of a 3D object based on its 2D projections. The reconstruction of a 3D vector field requires significantly more data than a conventional, scalar tomographic reconstruction because at each point in space a three-component vector is to be reconstructed, rather than a single scalar value; scalar tomography requires, as a minimum, a single tilt series for a complete 180° tilt range, whereas vector field electron tomography (VFET) requires four separate tilt series, each over a complete 180° tilt range. The input signal for VFET is the phase of the electron wave, so that for each tilt angle a phase reconstruction is required; this can be achieved either through electron holography or via the Transport-of-Intensity Equation (TIE) formalism. Alternatively, if a phase plate were available, it could be used to directly display the phase of the wave in the bright field image; after phase unwrapping, the reconstructed phases can then be used in the tomographic reconstruction.

In this contribution, we will describe two theoretical and numerical methods that can be used to reconstruct either the 3D magnetic induction in and around a magnetic object, or the 3D magnetic vector potential of this object. For the magnetic induction, \mathbf{B} , we make use of the vector form of the Fourier slice theorem, which relates the Fourier transform of a component of the magnetic induction to the magnetic component of the measured phase shift. This component is obtained from the difference of two phase maps, obtained with the incident beam along opposite directions. From the two pairs of tilt series, one can reconstruct two components of the magnetic induction, and the third component is recovered from the zero divergence condition on the magnetic induction. We will show through an analytical proof-of-concept derivation that the magnetic induction can be faithfully reconstructed from such a data set.

Alternatively, the phase data can be used to reconstruct the magnetic vector potential, \mathbf{A} , in the Coulomb gauge. We will once again provide a proof-of-concept derivation for this method, using the field of an elementary magnetic dipole as an example. It is somewhat surprising that the vector potential itself can be reconstructed directly, since the standard tomography literature states that only the curl of a vector field can be reconstructed (and $\text{curl}(\mathbf{A}) = \mathbf{B}$); we will show how this apparent discrepancy can be resolved by working in the Coulomb gauge.

We have applied both VFET algorithms to a number of model systems: uniformly magnetized sphere and rectangular prism, and various objects with closure domain structures. We will illustrate the results of these simulations, as well as preliminary experimental data. We propose a number of estimates of reconstruction errors and graphical methods to represent the 3D nature of the reconstructed vector fields.

Aberration Corrected Tilt Series Restoration

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Aberration correction compensates for distortions in a transmission electron microscope image introduced by the aberrations of the objective lens. Aberration correction can be performed either directly using non-round lenses or indirectly by image restoration from a series of images. Combining both types of aberration correction has additional advantages. Focal series restoration has previously been applied to aberration corrected images in order to improve the quality of aberration correction and retrieve the complex specimen exit wavefunction.

Unlike for focal series datasets, the resolution of a tilt series restoration is not limited to the axial information limit of the microscope as determined by the spatial and temporal coherence. In a conventional microscope the need to minimise oscillations in information transfer leads to a critical defocus condition for a given tilt. This limits the tilt angle that can be employed to $(\lambda/C_s)^{1/4}$ for a given electron wavelength (λ) and spherical aberration (C_s). In contrast, in an aberration corrected transmission electron microscope the value of axial coma is less sensitive to the illumination tilt angle and the tilt induced defocus change is smaller. The result is that the dataset for successful tilt series restoration under aberration corrected conditions is less reliant on optimal microscope stability and imaging conditions. Larger tilt angles up to 18 mrad can therefore be employed (c.f. optimal tilt angle of 3 mrad for an uncorrected microscope) so that greater resolution improvements are achievable.

To test the feasibility of aberration corrected tilt series restoration we have initially studied materials with well characterised atomic structures. Images were recorded using a JEOL JEM-2200FS C_s -corrected instrument operated at 200kV with a typical spherical aberration of -3 μm . In order to demonstrate that the information transfer of aberration corrected tilt series restoration is beyond the axial limit we have directly compared this approach with the axial focal series approach. Focal series comprised of 20 images separated by a focal increment of 10 nm with the series centered about the Gaussian focus condition. Tilt series consisted of short focal series taken at six different illumination tilts with tilt angles up to 18 mrad (c.f. optimal tilt angle of 3 mrad for an uncorrected microscope). For both datasets, specimen exit waves were restored under the linear imaging approximation using a Weiner restoring filter. The aberration measurements were locally refined to 3rd order for a specimen sub-region of interest using the phase correlation function / phase contrast index approach to an accuracy of <1 nm.

We will present successful aberration corrected tilt series restorations using a range of technologically significant ceramics including silicon and strontium titanate. We demonstrate that for tilt series restorations using tilts of 16mrad the information transfer limit of 10% corresponds to a spatial resolution of 0.075 nm. This demonstrates a greater than 50% improvement compared to the instruments axial 10% information limit, which restricts the linear information transfer of the focal series restoration to 0.12nm. Additional high spatial frequency lattice reflections are shown to be visible in the Fourier transforms of the restored tilt-series exit wavefunctions compared to the equivalent focal series data and extremely small atomic distances up to 78pm can be resolved in the phase of the restored tilt series.

TEM Imaging of NiFe_2O_4 Precipitates in NiO Using the LACSBI Method

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Oxide ceramic materials undergoing oxidation-reduction reactions have applications in solar-thermal hydrogen production and fuel-cell energy production among numerous other fields. The NiO- NiFe_2O_4 system is both technologically important and a model system for studying interfaces during such reactions. Previous transmission electron microscopy (TEM) investigations of such interfaces relied primarily on diffraction- and phase-contrast imaging mechanisms. High-resolution quantitative chemical information is necessary, however, for a full understanding of the kinetics of the reaction near the precipitate-matrix interface. Large angular convergence scanned beam illumination (LACSBI) permits acquisition of an incoherent signal with highly damped diffraction and phase contrast. The LACSBI method can be used in conjunction with either strong-beam bright-field (BF) / dark-field (DF) or energy-filtered (EF) TEM spectral imaging techniques to obtain quantitative incoherent structural or chemical images, respectively. We will present the results of BF-DF and EFTEM studies of NiFe_2O_4 particles in a NiO matrix using the LACSBI method. Preliminary results of tomographic studies using these imaging methods will also be presented.

Electron Energy Loss Spectroscopy of an Ultra-thin SrTiO₃/SrMnO₃/LaMnO₃ Film Superlattice

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We have investigated SrMnO₃ (SMO), LaMnO₃ (LMO), and SrTiO₃ (STO) thin films. SMO and LMO are typically insulators when grown epitaxially. At the interface of two oxides, the electronic properties are different from either bulk film [1]. When the films are grown very thin, the entire superlattice may adopt a new electronic structure due to every film being an interface. It is possible for the material to undergo insulator to metal transitions by changing the stoichiometry and/or film thickness.

Transition metal oxides films were grown on a <100> SrTiO₃ substrate by atomic-layer molecular beam epitaxy. Alternating thin films of SrTiO₃ (STO), SrMnO₃ (SMO), and LaMnO₃ (LMO) were grown at 700 °C. These perovskite films are closely lattice-matched. Approximately 70 nm of film was grown, with thicknesses of 1 – 4 unit cells (~ 4 -16 Angstroms). A JEOL JEM 2010F STEM/TEM was used to obtain annual dark field STEM images and EELS line scans of a cross sectional specimen.

In the O K spectra, we observe the O K edge shifts towards lower energy loss in LMO films. These LMO films are followed by a single layer of SMO and 3 layers of STO. Three of the LMO films are single layered and one is double layered. The oxygen bonding to transition metals is changing across the superlattice. Since the peak shift is larger in 2 unit cells of LMO than 1 unit cell, we conclude that the electronic structure of the LMO-SMO interface is dependent on film thickness. We also observe that the Mn L_{2,3} peak does not shift from LMO to SMO films. The Mn 2p edge allows one to determine the Mn valence [2]. These peaks relate to excitations of electrons from 2p to 3d states [2, 3, 4]. Since the near-edge structure is the same in LMO and SMO films, the valence is not changing, even though the bulk valence of Mn in LMO and SMO is +3 and +4 respectively. Additionally, there is a peak shift of the O K prepeak towards lower energy loss in SMO films in a 3 x 3 SMO-STO superlattice. The O K prepeak is strong in STO films and weaker elsewhere.

The structure of the film are characterized by nanoarea electron diffraction with a probe size of 40 nm in diameter. We observed both superlattice reflections and shift in the Bragg peak positions. The lattice distortions are measured from the Bragg peak positions. The combination of local electronic structure and structure determinations allow a correlation between the two properties.

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Scanning Confocal Electron Microscopy Image Calculation Based on Bloch Wave Method

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Scanning Confocal Electron Microscopy (SCEM) which is analogous to optical confocal microscopy was proposed by N. J. Zaluzec, and investigated by Frigo et al[1], observing relatively thick semi-conductor device samples for its 3D imaging capability. A focused probe is formed by upper lens and the scattered electrons are focused by lower lens and corrected by a detector placed at real space. Recent progress in aberration correction technique for scanning transmission electron microscopy (STEM) provides a localized probe also in z-direction that makes SCEM a higher resolution 3D imaging. However, recent study shows[2] that the image intensity is difficult to intuitively relate to the structure therefore an understanding of the image formation mechanism, and an effective image calculation technique is necessary. Nellist et al[3], suggested an efficient STEM calculation technique based on Bloch wave method. This technique provides not only fast calculation method, but also a good perspective of physical picture of the imaging. In this work, Bloch wave based image simulation method for SCEM is presented based on Nellist's calculation technique.

In the Nellist's method, Fourier components of the image are calculated in matrix form. For the SCEM, it was proven to be expressed as following:

$$\tilde{I}(\mathbf{Q}_0, z) = \int d\mathbf{K}_{\parallel f} \int d\mathbf{K}_{\parallel} \left[\mathbf{A}_{\mathbf{K}_{\parallel}+\mathbf{Q}}^* [\Phi \Gamma \Phi^{-1}]_{\mathbf{K}_{\parallel}+\mathbf{Q}}^+ \mathbf{B}_{\mathbf{K}_{\parallel}+\mathbf{Q}}^* \right]_{\mathbf{K}_{\parallel}} \frac{(-2\pi r_D) J_1(|\mathbf{K}_{\parallel f} - \mathbf{K}_{\parallel}'| \cdot r_D)}{|\mathbf{K}_{\parallel f} - \mathbf{K}_{\parallel}'|} \left[\mathbf{B}_{\mathbf{K}_{\parallel}} [\Phi \Gamma \Phi^{-1}]_{\mathbf{K}_{\parallel}} \mathbf{A}_{\mathbf{K}_{\parallel}} \right]_{\mathbf{K}_{\parallel}} \quad (1)$$

where, $\tilde{I}(\mathbf{Q}_0, z)$ is the Fourier components of the image, A, and B are the matrices expressing phase shift due to upper and lower lenses, respectively, $\Phi \Gamma \Phi^{-1}$ are the matrices of eigen values and eigen vectors of the system, and J_1 is the Bessel function due to the detector placed at real space. It is revealed that the image is formed by electrons with different incident directions mixed with the Bessel function characterized by the detector. The detail of the formalism and the simulation results are given in the presentation.

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Wavelength Dispersive X-Ray Spectroscopy of Thick and Thin Samples for Electron Microscopes

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Recent development of parallel beam X-ray spectrometers that use multi-capillary X-ray (MCX) optics to collimate divergent X-rays has made it possible to perform wavelength dispersive X-ray spectroscopy (WDS) easily in electron microscopes [1]. Since parallel beam spectrometers use flat crystals and simple θ - 2θ scanning system instead of curved crystals and Rowland circle mountings, they are compact and generate less vibration and noise. These characteristics make parallel beam spectrometers fit to use in scanning electron microscopes (SEMs) or in transmission electron microscopes (TEMs) for analysis which has been difficult to perform with energy dispersive X-ray spectroscopy (EDS). Using a MCX-WDS system (SHIMADZU) attached to a SEM (JEM-7000F, JEOL), we achieved light element analysis down to B for both bulk and TEM thin film samples with high energy resolution [2].

In the present study, we carried out light element analysis such as B, C, N, and O as well as elemental mapping using this SEM-WDS system. The system has 4 analyzing flat crystals (LiF, PET, RAP, and PbST) which cover energy range from 135eV to 10keV. Series of samples, boron compounds (h-BN, and B₄C), carbon or its compound (graphite, and 6h-SiC), and oxides (α -Al₂O₃, and SiO₂ (α -quartz)), were analyzed. For most experiments, primary electron energy of 15 keV was used at about 200 nA current. The energy resolutions measured from B-K peak of h-BN (using the PbST crystal) and O-K peak of Al₂O₃ (using the RAP crystal) are 6.0eV and 4.5eV, respectively.

The B-k peak of B compounds represented their bonding states. While h-BN has the graphite structure with less anisotropy, the crystal structure of B₄C is composed of B₁₁C icosahedra linked by C-B-C chains [3]. Thus, the B-K peak of h-BN corresponded to combination of B-N π and σ states, and that of B₄C was mainly from B-C π states. The second diffraction spectra were measured for graphite and 6h-SiC samples for better resolution. The C-K peak shape of graphite has clear shoulders which correspond to C-C π and σ states, but that of SiC is mostly composed of Si-C σ states. Al₂O₃ and SiO₂ have same SiO₄ tetrahedron although detailed crystal structure is different. Here both oxides showed almost the same peak shapes but with a peak shift representing the difference of ion diameters of Al and Si. These basic results suggest that the present SEM-WDS system has enough capability to analyze light elements for both bulk and thin film specimens with high resolution. The result of WDS mapping of inorganic and organic samples will also be presented.

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Nanoscale STEM Tomography and Elemental Analysis of a Multiferroic Material

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Three-dimensional (3D) electron microscopy has been used successfully in the biological sciences for cells, viruses and other biological materials, primarily using bright-field TEM. However, for crystalline samples, the problem of dynamic diffraction contrast challenges the monotonic relationship between the image contrast and the thickness of sample. Instead, an alternative tomography method, high angle annular dark field (HAADF) STEM tomography, can hold this linearity due to its incoherent nature in the image formation. In STEM, the images are formed by collecting the high angle scattered electron on an annular dark field detector. The nature of the scattering leads to an incoherent signal, which is sensitive to changes in specimen thickness and atomic number, forming the so-called Z-contrast image.

In recent years, there have been tremendous interests in the multiferroic materials that display a spontaneous magnetization with a ferroelectric polarization. Strong coupling between the polarization and magnetization in the materials enables their potential applications in information storage and spintronics devices. More recently, Baettig and Spaldin used first principles density functional theory to study a new multiferroic material, namely $\text{Bi}_2\text{FeCrO}_6$ (BFCO) and predicted much larger ferromagnetic and ferroelectric properties than those of the known multiferroic materials. However, few successful synthesis and measurement of multiferroic properties of this hypothetical material have been reported. In this paper, a sol-gel processing method was used to synthesize the nanopowder of BFCO at 1000 degree C. The structure and chemistry of the nanopowder was characterized using a 200kV Schottky field-emission gun (FEG) FEI Tecnai F20-ST STEM/TEM microscope. The result showed that the nanoparticles of Bi-based compounds with a feature as small as 1-2 nm can be resolved in 3D by STEM tomography. The chemical composition of individual nano-particles was analyzed using EDX spectroscopy and EELS simultaneously with STEM imaging. The 3D data of the nanoparticles were successfully reconstructed to illustrate the distribution and morphology of the nanoparticles.

The tomography acquisition and reconstruction was performed using an Xplore 3D Tomography package at the North America Nanoport of FEI Company. The authors thank the support from the applications team, especially Y-C Wang, of FEI Company.

Characterization of Complex Bainite Microstructure in Low Carbon HSLA Steels Using FIB and TEM

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The austenite phase observed in low carbon HSLA steels is well known to be decomposed to various bainitic microstructures, such as granular bainite, acicular ferrite and bainitic ferrite, during continuous cooling process. These bainitic microstructures have been usually identified by using either scanning electron microscope (SEM) or transmission electron microscope (TEM). However, SEM and TEM images do not exactly coincide, because of the quite different sample preparation method in SEM and TEM observations. These conventional analysis method is, thus, not suitable for characterization of the complex bainitic microstructure.

In the present study, focused ion beam (FIB) technique was applied to make site-specific TEM specimens and to identify the 3-dimensional grain morphologies of bainitic microstructure in low carbon HSLA steels. Granular bainite consisted of fine subgrains and 2nd phase constituents like M/A or pearlite located at both grain and subgrain boundaries. Acicular ferrite was characterized by an aggregate of randomly orientated and irregular shaped grains. The high angle relation between adjacent acicular ferrite grains was thought to be caused by intragranular nucleation during continuous cooling process. Bainitic ferrite revealed uniform and parallel lath structure within the prior austenite grain boundaries and 2nd phase constituents such as M/A or martensite located at lath boundaries.

Band-Gap Measurements Using Electron Energy-Loss Spectroscopy

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Until recently the natural energy spread of the electron emitter represented the limiting factor for the energy resolution in electron energy-loss spectroscopy. Apart from deconvolution techniques [1], it is in particular the recent implementation of monochromators into transmission electron microscopes which has allowed breaking this limitation. This opens new possibilities for material characterization by electron energy-loss (EEL) spectroscopy (e.g.,[2]). The present results are obtained with the Zeiss LIBRA 200FE and SESAM microscopes which are equipped with an electrostatic Omega-type monochromator (produced by CEOS) and highly dispersive energy filters.

The zero-loss spectrum acquired in the SESAM with the smallest energy-selecting monochromator slit and an acquisition time of 10 s exhibits a full width at half maximum (FWHM) of 87 meV. Apart from the small FWHM, the slope of the “zero-loss” tail is large which is important because it is this tail which extends well beyond the FWHM range and thus interferes with the low-loss part of the EEL spectrum. After subtraction of the tail, the onset of electron excitations from the top of the valence band to the bottom of the conduction band in semiconductors and insulators is unambiguously visible. Examples were obtained from a series of different semiconductors from the GaN–AlN system, diamond, and Si. Differences are clearly noticeable which are due to the different band gaps and the variation of the band structure. The noise level of the spectra is very low because of the long exposure time which allows detection of subtle details.

Cerenkov radiation (CR), transition radiation (TR), and surface plasmon losses can interfere with the onset of the band gap. By varying specimen thickness and detected scattering angles we minimized the influence of these artefacts. For the direct semiconductor GaN we found that below a critical specimen thickness CR and TR are negligible and also surface losses are small. In the case of the indirect semiconductor Si we used electrons scattered to large angles. Under these conditions indirect transitions are strongly enhanced and Cerenkov losses are completely removed because they are limited to a very narrow angular range [3]. Limitations of spatial resolution and possible solutions for improvements will be discussed.

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Atomic Scale Analysis of Nitrogen Distribution in GaAsN Quantum Wells

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The ability to vary the energy gap and strain levels through minute composition changes, and thus tailor advantageous band structures, has made III-V semi-conductor alloys a material of choice for optoelectronic device research. Of particular interest is the quaternary system GaInNAs, wherein the addition of small amounts of nitrogen to GaInAs can generate large band gap bowing effects whilst barely affecting the lattice parameter of the alloy. Recent studies of GaInAs/GaInNAs heterostructures have revealed the presence of a particular type of defect uncharacteristic of the GaInAs system, likely therefore to result from the introduction of nitrogen into the matrix. Understanding the behaviour of N doping atoms in GaAs is therefore essential if one is to preserve the structural integrity and optical properties of the functional quaternary alloy.

Observations of low nitrogen concentration GaNAs quantum wells in a GaAs matrix with high angle annular dark field (HAADF) imaging have however brought to light a remarkable behaviour. The nitrogen-rich quantum wells appear brighter in the HAADF images than their surrounding GaAs matrix. In the commonly accepted picture of fully substitutional nitrogen doping, whereby each N atom replaces an As atom, the GaAs matrix is heavier than the doped wells and the sensitivity of HAADF to the atomic number of the imaged elements would have led to expect the opposite contrast. A thorough atomic resolution study of the contrast differences between doped and un-doped areas as a function of nitrogen concentration was carried out on an aberration-corrected VG HB501 dedicated STEM. Factors such as specimen thickness variations around the well and the influence of the camera length were also considered to build the most complete picture to date of this system. The initial comparison of the experimental images to simulations of fully relaxed theoretical structures elucidates the observed contrast and sheds new light on what could be thought of as strain contrast in HAADF. It also appears that one may be able to distinguish between the substitutional or interstitial nature of the nitrogen doping atoms, and more specifically which particular type of nitrogen-induced defect complexes forms in epitaxial GaAs.

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Hydrogen Encapsulation Properties of Type-I Silicon Clathrate Compounds: Aberration-Corrected Z-Contrast Studies of the Structure of $\text{Na}_x\text{Si}_{46}$ and K_xSi_{46} .

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In the quest for alternative energy sources, hydrogen has long been touted as one of the most likely candidates to replace fossil fuels, provided practical solutions for its storage and transport can be found. Amongst other nano-porous materials such as zeolites, clathrate hydrates have shown remarkable potential for hydrogen storage, adsorbing up to 7.5% wt hydrogen, albeit in extreme pressure and temperature conditions. Upon crystallising, these compounds form a three-dimensional host matrix where guest atoms can be accommodated within distinct polyhedral “cages”. Unlike their hydrate counterparts, however, silicon and germanium based inorganic clathrates had until now mostly been studied for their superconductivity and thermoelectric behaviour. The present work nevertheless exhibits two metal silicide clathrates, stable at room temperature, with promising hydrogen encapsulation properties.

The type-I silicon clathrate consists of a silicon matrix with two distinct guest sites, labelled $2a$ and $6d$, occupied most commonly by alkali or alkali earth metal atoms. Magic angle spinning nuclear magnetic resonance has confirmed that, in the case of Na guest atoms and in the growth conditions specific to this work, the guest sites are Na deficient and H rich. The precise structure and stoichiometry of the resulting compound was subsequently investigated by aberration-corrected Z-contrast imaging. When observed in (001) projection, the $6d$ guest site, at the centre of the larger of the two polyhedral cages, is nicely isolated from neighbouring atoms. This allows the unequivocal determination of its occupancy through quantitative comparison with simulated images. In the case of $\text{Na}_x\text{Si}_{46}$, it emerged that a third of the $6d$ sites were Na-deficient and thus H-rich, yielding a stoichiometry consistent with the energy-dispersive X-ray (EDX) analysis of the compound. A similar investigation of the K_xSi_{46} type-I clathrate revealed that in the case of potassium guests only a fifth of the large $6d$ cages were K-deficient, whilst some of the smaller $2a$ sites had to be deficient as well to explain the EDX results. Rotating the structure into higher index zone axes to project the $2a$ sites into different positions indeed confirmed these earlier findings. Due to the high precision needed for the analysis, great care was taken to decouple thickness effects and the contribution from neighbouring columns from the $2a$ site contrast in the images. This was achieved by combining information from simultaneous bright field and dark field imaging, in what is probably one of the first practical demonstrations of the great potential of integrating bright field techniques in quantitative aberration-free STEM analysis.

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In-Situ Focused Ion Beam (FIB) Microscopy at High Temperature

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Materials Scientists need information on the kinetics of the microstructural evolution processes that determine the finished microstructure, and hence the properties, of any material. E.g. recrystallisation, grain growth and phase changes. Such kinetic information requires reliable discrimination of differently oriented crystallites, different crystal phases and/or elemental concentration changes coupled with useful spatial resolution and temporal resolution (i.e. high frame rates). These imaging results must be realised from a hot and changing specimen, in an instrument that is compatible with that hot specimen and with a practical specimen heater. Focused Ion Beams (FIB) offer strong contrast between crystallites and phases, and hence offer the ability to discriminate between these features even while imaging at fast frame rates, however their compatibility with hot specimens was unproven. Here we report results from a novel combination of FIB with an in-situ heating stage, to produce in-situ, real-time microstructural moving images from a variety of metallic specimens at temperatures up to about 700°C.

We show that the use of FIB with hot specimens is practical and gives better contrast than backscattered electron channelling/orientation contrast in the SEM. We also show that the site-specific milling capabilities of FIB are useful in preparing and maintaining a flat, stress-free surface on soft or otherwise “difficult” materials and that ion beam scanning can suppress the formation of thermally etched grooves at grain boundaries. However, we also show that use of Ga⁺ ions limits the usable temperature range by deposition of either liquid gallium or solid gallium oxide onto the specimen at temperatures above about 700°C. Use of Ga⁺ also renders the technique incompatible with aluminium alloys. The total amount of material eroded over the course of a 3+ hour grain growth experiment is in the order of tens of nanometres, compared to a finished grain size of tens or hundreds of micrometres.

We propose a measure of “Megapixels per second” in preference to the more intuitive “frames per second” as a quantitative measure of temporal resolution when comparing different dynamic in-situ imaging techniques. This avoids the difference in frame sizes and scan speeds between different techniques and different implementations of the same technique. This measure also allows users and prospective users to estimate in advance appropriate compromises between temporal and spatial resolution for any given application.

Electronic and Atomic Structures of Thin Film Perovskite Vanadates

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Vanadium-based perovskites ($\text{AVO}_{3-\delta}$) have attracted increasing interest in recent decades because they form a model system for systematically studying the correlation of structure and properties of transition metal oxides. The cubic based perovskite structures of $\text{AVO}_{3-\delta}$ can be varied by taking different A cations, which then results in different physical properties, such as electronic, magnetic and ferroic properties. To understand the mechanism of this property-structure relationship, the correlation between electronic and crystal structures of the perovskites must be studied. Electron energy loss spectroscopy in a scanning transmission electron microscopy offers distinguished opportunities on this type of study since it allows simultaneous imaging and spectroscopy analysis.

In this work, the correlation between the electronic and atomic structures of several typical $\text{AVO}_{3-\delta}$ thin films and the interfaces with their substrates was investigated by EELS and STEM. The studied perovskite vanadate thin films include $\text{SrVO}_{3-\delta}$ (SVO), PbVO_3 , $\text{CaVO}_{3-\delta}$ (CVO), $\text{LaVO}_{3-\delta}$ (LVO) and $\text{YVO}_{3-\delta}$ (YVO), which were grown on single-crystalline LaAlO_3 or SrTiO_3 substrates by Pulsed Laser Deposition (PLD). Crosssection TEM specimens were prepared for microscope observation.

The present work focuses on: oxidation state determination of V in thin films and at their interfaces; atomic structure of interfaces and their electronic structures; inter-diffusion and the resulted variation of transport properties across the interfaces. Several methods for determining oxidation states by EELS have been compared and evaluated. The result shows that it is reliable to determine the valence of V in perovskite vanadates by combining white-line intensity ratio and the energy loss near edge structures (ELNES) of V-L edges. The oxidation states of V in our thin films are 4+ in SVO and 3+ in YVO and LVO. However, the oxidation states of V in PVO and CVO deviate from 4+ according to the white line intensity ratio calculation. Further investigation reveals that these deviations are from the existence of oxygen vacancies for PVO and surface effect for CVO. Extra electrons have been revealed at the interface of SVO/LAO although the interface is atomically smooth and free of inter-diffusion. The existence of extra electrons can be mainly attributed to the bonding of V-O with La-O layers and this explanation has been confirmed by high resolution Z-contrast imaging and theoretical calculations. Comparatively, the interface of CVO/STO is more complicated due to the presence of mismatch dislocations. The fine structures of both V-L and Ti-L change significantly at the interface with respect to those of bulks. These mainly result from the coordination variation and electronic reconstruction at the interface. A detailed description and discussion will be presented, and the results from other vanadates will be compared.

Results of a pnCCD Detector for Direct Single-Electron Imaging in the TEM

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Electron microscopy, especially cryo-electron microscopy is widely applicable for structural investigations in the soft materials and life sciences. However, these types of specimen, *e.g.*, organic / polymer electronics, polymer nanocomposites and, generally all frozen hydrated biological samples are highly sensitive to electron beam radiation. To overcome this major limitation low-dose techniques have to be used, distributing the total electron dose to many single images, demanding highly sensitive recording devices. Phosphor-coated fiber coupled CCD cameras are typically used where the primary electrons are converted to visible light. This indirect detection strategy is characterized by significant levels of readout and dark-current noise. Additionally, the number of optical interfaces within the entire camera assembly results in multiple scattering and a subsequent loss in resolution. Since the total applied dose can't be increased in such beam sensitive studies, the improvement in camera performance with noise-reduced recording, a higher sensitivity, and at the same time higher spatial resolution is therefore definitely beneficial for low-dose applications.

In this investigation we characterize a pnCCD detector that is highly suitable for direct single-electron detection in the TEM. The first detector tested is a 132x264 50µm-pixel array, cooled to -30°C and it was tested on a Philips CM12 at 120kV. A sharp knife-edge was placed directly on top of the pixel array, such that the LSF, MTF, NPS and DQE could be evaluated properly. Additional imaging and sensitivity measurements were conducted and preliminary results show that the novel detector is highly sensitive such that ultra-low dose experiments are feasible.

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Measurement of Residual Stress by Using the Focused Ion Beam and Digital Imaging Correlation Method in NiCrAlY Thermal Spray Coatings

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Thermal spray coating has high deposition efficiency and the coating layer reveals dense structure. However, residual stress is induced during thermal spray coating process resulting in the degradation of mechanical properties in coating layer. The exact measurement of residual stress of thermal coating layer, thus, is very important. X-ray diffraction (XRD) method and layer removal method have been applied to measure the residual stress of coating layer. These methods, however, have disadvantages such as difficulty in sample preparation and high error range. Therefore, it is worthy to find the easy and reliable method in measuring the residual stress of coating layer. In present study, the attempt to measure the residual stress in coating layer has been tried by using the combination of the focused ion beam (FIB) milling and high resolution strain mapping program (VIC-2D). At first, a slot was introduced by FIB milling with low energy beam and the displacement was obtained by the digital correlation analysis of high-resolution scanning electron micrographs. The residual stress can be determined by fitting of the experimental results to an analytical value. The FIB-DIC method has been successfully applied to coating layer. FIB-DIC method has a high accuracy level from experimental results.